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

The Pinacol–Pinacolone Rearrangement. VI. The Rearrangement of Symmetrical Aromatic Pinacols

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In continuation of our studies on the pinacol–pinacolone rearrangement,[2] we have prepared ten symmetrical aromatic pinacols of the type $R_1R_2C(OH)(HO)CR_2R_1$ and have subjected them to rearrangement. We were particularly interested in pinacols containing the *p*-ethoxyphenyl (phenetyl) and *m*-methoxyphenyl groups in order to obtain the migration aptitudes of these groups. Bachmann and Moser[3] found that it is possible to predict quantitatively the extent to which two groups R_1 and R_2 will migrate in the pinacol $R_1R_2C(OH)(HO)CR_2R_1$, if one knows the relative migration aptitude of each group with respect to a mutual third group R; they reported six cases in which the predicted values agreed very well with the actual experimental results. Accordingly, we have chosen such pinacols as would allow us to test their conclusion that the rearrangement of symmetrical pinacols is dependent only on the migration aptitudes of the groups. In Table I is shown the extent of migration of each of the groups present in the pinacols which were studied in this investigation.

TABLE I

MIGRATION OF GROUPS IN SYMMETRICAL AROMATIC PINACOLS

$R_1R_2C(OH)(HO)CR_2R_1$

Groups		Migration, %	
R_1	R_2	R_1	R_2
Phenetyl	Phenyl	98.3	1.7
Phenetyl	*p*-Tolyl	97	3
m-Methoxyphenyl	Phenyl	38	62
m-Methoxyphenyl	*m*-Tolyl	39	61
Anisyl	*m*-Tolyl	99	1
p-Chlorophenyl	Anisyl	1	99
p-Chlorophenyl	*p*-Tolyl	1.7	98.3
m-Methoxyphenyl	*p*-Tolyl	10	90
m-Methoxyphenyl	*p*-Biphenyl	13.5	86.5
m-Chlorophenyl	*p*-Biphenyl	0	100

From these values the migration aptitude of the phenetyl group with respect to the phenyl group as unity is found to be approximately 500; this value is calculated from the fact that the phenetyl group migrates 32 times as fast as the *p*-tolyl group which in turn migrates 15.7 times as rapidly as the phenyl group. It is considered that the value 32 × 15.7 is a more accurate measure of the migration aptitude of the phenetyl group than that obtained by direct comparison of the phenetyl and phenyl groups (98.3/1.7 = 58), because a slight error in the determination of the latter relation affects the ratio to a marked extent. For a similar reason the revised value of 500 is given to the anisyl group in place of 70+, which has been reported.

By direct comparison of the *m*-methoxyphenyl group with the phenyl group a value of 0.6 is obtained for the migration aptitude of the *m*-methoxyphenyl group. We have been unable to determine, as yet, whether this result is valid inasmuch as there remains some question concerning the nature of the triarylmethane which is formed in the cleavage reaction of the pinacolones with alkali. Bailar[4] has reported a value of 0.2. The values for the migration aptitude of the *m*-methoxyphenyl group obtained by comparison with the *p*-biphenyl group, the *p*-tolyl group and the *m*-tolyl group are 1.79, 1.74 and 1.25, respectively, the average of the three being 1.6; tentatively, this average value is used to represent the migration aptitude of the *m*-methoxyphenyl group.

The complete series of migration aptitudes of aryl groups to date is as follows: anisyl, 500; phenetyl, 500; *p*-tolyl, 15.7; *p*-biphenyl, 11.5; isopropylphenyl, 9; *p*-ethylphenyl, 5; *m*-tolyl, 1.95; *m*-methoxyphenyl, 1.6; phenyl 1.0; *p*-iodophenyl, 1.0; *p*-bromophenyl, 0.7; *p*-chlorophenyl, 0.66; *o*-methoxyphenyl, 0.3; *m*-bromophenyl, *m*-chlorophenyl, *o*-bromophenyl, *o*-chlorophenyl, 0. It is apparent that the position occupied in the benzene ring is of importance; the para position engenders the greatest migration aptitude, the meta position less and the ortho least.

Kharasch and co-workers[5] determined the electronegativity of groups and have arranged the aryl radicals in the following order of decreasing

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[1] Submitted in partial fulfilment of the requirements for the Ph.D. degree.

[2] V. Bachmann and Sternberger, THIS JOURNAL, **56**, 170 (1934).

[3] Bachmann and Moser, *ibid.*, **54**, 1124 (1932).

[4] Bailar, *ibid.*, **52**, 3596 (1930).

[5] Kharasch and Marker, *ibid.*, **48**, 3130 (1926); Kharasch and Flenner, *ibid.*, **54**, 674 (1932).

electronegativity: anisyl, *o*-methoxyphenyl, *o*-tolyl, *m*-tolyl, *m*-methoxyphenyl, phenyl, *p*-chlorophenyl, *o*-chlorophenyl, *m*-chlorophenyl. The series is similar to that of the migration aptitudes only if the ortho substituted groups are neglected; the ortho groups have a high electronegativity but possess little tendency to migrate.

Prediction of Migration of Groups.—The method of predicting the relative migration aptitudes of two groups R_1 and R_2 from the values of the relative migration aptitudes of these groups with respect to a mutual third group has been described previously.[3] In Table II the experimental results are compared with the calculated values for the pinacols studied in this work.

TABLE II

COMPARISON OF PREDICTED AND ACTUAL MIGRATION OF GROUPS

Groups		Mutual	Migration, %			
			Calcd.		Found	
R_1	R_2	group R	R_1	R_2	R_1	R_2
Phenetyl	Phenyl	(*p*-Tolyl)	99.8	0.2	98.3	1.7
m-Methoxyphenyl	*p*-Tolyl	(*p*-Biphenyl)	10	90	10	90
Anisyl	*m*-Tolyl	(Phenyl)	99.5	0.5	99	1
m-Methoxyphenyl	*m*-Tolyl	(*p*-Biphenyl)	47	53	39	61
p-Chlorophenyl	Anisyl	(Phenyl)	0.2	99.8	1	99
p-Chlorophenyl	*p*-Tolyl	(Phenyl)	4	96	2	98
m-Chlorophenyl	*p*-Biphenyl	(Phenyl)	0	100	0	100

It is seen that the predicted values agree satisfactorily with the experimental results. These results confirm the conclusion of Bachmann and Moser that in symmetrical aromatic pinacols the rearrangement depends entirely on the character of the groups.

Experimental

4-Ethoxybenzophenone.—This ketone was prepared by the Friedel and Crafts reaction in 83% yield from benzoyl chloride and phenetole; after distillation and recrystallization from ligroin, the colorless needles of the ketone melted at 47° while the reported value is 38–39°.[6]

Anal. Calcd. for $C_{13}H_9O(OC_2H_5)$: OC_2H_5, 19.9. Found: OC_2H_5, 19.8.

4-Ethoxy-4′-methylbenzophenone.—This new ketone was obtained by adding 35 g. of aluminum chloride in portions to 23.3 g. of *p*-tolyl chloride and 25 g. of phenetole in 225 cc. of carbon disulfide. After standing twelve hours at room temperature, the mixture was refluxed for half an hour and then hydrolyzed. The ketone was purified by distillation (b. p. 207–217° at 13 mm.) and recrystallization from alcohol from which it separated in colorless needles; m. p. 84–85°; yield, 33.5 g. (93%).

Anal. Calcd. for $C_{14}H_{11}O(OC_2H_5)$: OC_2H_5, 18.7. Found: OC_2H_5, 18.5.

3-Methoxybenzophenone.—A 77% yield (17.1 g.) of this ketone was obtained by adding a solution of 13.3 g. of 3-methoxybenzonitrile in 13 cc. of ether to the Grignard reagent from 19 g. of bromobenzene in 50 cc. of ether. After being heated for one hour, the mixture was kept at 0° for a day; the solid addition product which precipitated was filtered off, washed with ether–ligroin (1:1) and then heated with dilute hydrochloric acid in order to hydrolyze the ketone-imine. After recrystallization from ligroin or distillation (b. p. 185° at 4 mm.) the 3-methoxybenzophenone melted at 38–40°. Ullmann and Goldberg[7] who prepared this ketone by the Friedel and Crafts reaction reported a melting point of 37°.

3-Methoxy-3′-methylbenzophenone.—A mixture of 20 g. of 3-methoxybenzonitrile and the Grignard reagent from 31 g. of *m*-bromotoluene in 80 cc. of ether was refluxed for an hour, cooled and hydrolyzed. By distillation (b. p. 190–200° at 12 mm.) the ketone was obtained as a nearly colorless liquid; yield, 22 g. (65%); the pure ketone boils at 212–213° at 22 mm.

Anal. Calcd. for $C_{14}H_{11}O(OCH_3)$: OCH_3, 13.7. Found: OCH_3, 13.4.

4-Methoxy-3′-methylbenzophenone.—This new ketone was prepared in two ways: by the Grignard reaction from 4-methoxybenzonitrile and by oxidation of 4-methoxy-3′-methylbenzohydrol.

To the cooled Grignard reagent from 41 g. of *m*-bromotoluene in 100 cc. of ether was added a solution of 26 g. of 4-methoxybenzonitrile in 30 cc. of ether. After one hour of refluxing the mixture was hydrolyzed. By distillation (b. p. 238–240° at 35 mm.) the ketone was obtained as a nearly colorless liquid; yield 34.9 g. (79%).

Anal. Calcd. for $C_{14}H_{11}O(OCH_3)$: OCH_3, 13.7. Found: OCH_3, 13.5.

4-Methoxy-3′-methylbenzohydrol.—Anisaldehyde (28 g.) was added drop by drop to the Grignard reagent from 42 g. of *m*-bromotoluene in 125 cc. of ether; throughout the addition the temperature was kept below 10°. The clear solution was kept at 0° for a day in order to allow the bromomagnesium salt of the hydrol to precipitate completely. The solid was filtered off and hydrolyzed; the hydrol was recrystallized from a mixture of benzene and petroleum ether from which it was obtained in the form of broad colorless needles; yield, 26 g. (55%); m. p. 51–52°. The 4-methoxy-3′-methylbenzohydrol is extremely soluble in benzene, fairly soluble in alcohol and little soluble in petroleum ether.

Anal. Calcd. for $C_{14}H_{13}O(OCH_3)$: OCH_3, 13.6. Found: OCH_3, 13.0.

Oxidation of the hydrol to the ketone was accomplished by adding a solution of 4.2 g. of chromic anhydride in 5 cc. of water and 15 cc. of acetic acid to a solution of 14 g. of 4-methoxy-3′-methylbenzohydrol in 25 cc. of acetic acid at room temperature. After standing overnight the mixture was poured into water; the oily ketone was purified by distillation; yield, 11.5 g. (82%).

3-Chloro-4′-phenylbenzophenone.—To 39 g. of *m*-chlorobenzoyl chloride and 40 g. of biphenyl in 300 cc. of

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(6) Gattermann, Ehrhardt and Maisch, *Ber.*, **23**, 1206 (1890).

(7) Ullmann and Goldberg, *ibid.*, **35**, 2813 (1902).

carbon disulfide was added 55 g. of aluminum chloride in portions; the mixture was refluxed on a steam-bath overnight and then hydrolyzed. The ketone was purified by distillation (b. p. 225–260° at 4 mm.) and recrystallization from alcohol; from this solvent the 3-chloro-4′-phenylbenzophenone crystallized in clusters of colorless plates; yield, 42.3 g. (65%); m. p. 106–107°. The ketone is very soluble in acetone, benzene and chloroform when hot, and is fairly soluble in these solvents at room temperature.

Anal. Calcd. for $C_{19}H_{13}OCl$: Cl, 12.1. Found: Cl, 12.0.

3-Chloro-4′-methylbenzophenone.—This ketone was prepared in the manner described for 3-chloro-4′-phenylbenzophenone, except that toluene was substituted for biphenyl. The 3-chloro-4′-methylbenzophenone was obtained in glistening colorless plates by recrystallization from benzene; yield, 56%; m. p. 97–98°.

Anal. Calcd. for $C_{14}H_{11}OCl$: Cl, 15.4. Found: Cl, 15.5.

The mixture was diluted with water and the insoluble material was filtered off and washed with water and with alcohol. The pinacol was extracted from the dried product by means of benzene or chloroform.

Reduction of ketones by the mixture Mg + MgI_2 was carried out as described previously.[8] In agreement with the work of Gomberg and Bachmann, it was found that in the reaction colored solutions were obtained of the equilibrium mixture of iodomagnesium pinacolate and colored iodomagnesium ketyl radicals. The quantity of metallic magnesium that reacted with the ketone corresponded to the theoretical amount. Ketones containing alkoxyl groups gave poor yields in this reaction.

Photochemical reduction was accomplished by exposing a solution of 5–10 g. of ketone in 100 cc. of isopropyl alcohol to sunlight for one to two months.

The essential data are given in Table III. The yields are based on recrystallized product; in many cases the yield of crude product was nearly quantitative but large losses were incurred during the process of recrystallization.

TABLE III

YIELDS AND PROPERTIES OF THE PINACOLS

sym-Benzopinacol	Yield, %			M. p., °C.	Cryst. form	Color with C_2H_5ONa	Analyses, %			
	Zn + AcOH	Mg + MgI_2	Photo-chem.				Calcd. C	Calcd. H	Found C	Found H
4,4′-Diethoxy-[a]	53	27	70	141–142	Needles	Blue	79.2	6.7	78.5	7.0
4,4′-Diethoxy-4″,4‴-dimethyl-	33	22	28	168–169	Prisms	Green-blue	79.6	7.1	78.9	7.1
3,3′-Dimethoxy-[b]	40	20	74	140–142	Cubes	Blue				
3,3′-Dimethoxy-4″,4‴-dimethyl-	64		78	160–162	Prisms	Green	79.2	6.7	78.3	6.8
3,3′-Dimethoxy-4″,4‴-diphenyl-		45		172–173	Needles	Green	83.0	5.9	82.6	6.6
3,3′-Dimethoxy-3″,3‴-dimethyl-	32		26	139–140	Granules	Green	79.2	6.7	79.6	6.8
4,4′-Dimethoxy-3″,3‴-dimethyl-[c]	37		17	144–145	Needles	Blue	79.2	6.7	78.6	6.7
4,4′-Dimethoxy-4″,4‴-dichloro-[d]				181–182	Diamond plates	Green-blue	Cl:	14.3	Cl:	14.4
4,4′-Dichloro-4″,4‴-dimethyl-[e]						Green				
3,3′-Dichloro-4″,4‴-diphenyl-		77		174–175	Needles	Green	Cl:	12.1	Cl:	12.1

[a] The pinacol was obtained in 41% yield by the interaction of 4.6 g. of benzil and the Grignard reagent from 20 g. of *p*-bromophenetole in 90 cc. of ether and 20 cc. of benzene; the reaction mixture was kept cold at first, then refluxed for one-half hour. [b] Bailar[4] reported a melting point of 139° for this pinacol. [c] This pinacol was prepared also by the Grignard reaction; to an ice-cold Grignard reagent from 6.8 g. of *m*-bromotoluene in 20 cc. of ether and 20 cc. of benzene was added 2.7 g. of anisil in portions; hydrolysis of the mixture after two days at room temperature yielded 2.1 g. (46%) of the pinacol. [d] A 47% yield of this pinacol was obtained by reaction of 5.4 g. of anisil with cold Grignard reagent from 15.3 g. of *p*-chlorobromobenzene in 40 cc. of ether and 50 cc. of benzene; the mixture was hydrolyzed after standing for two days at room temperature. [e] This pinacol has been prepared previously by the magnesium–magnesium iodide reaction; we have prepared it also by adding 1.8 g. of *p*-tolil to the Grignard reagent from 5.7 g. of *p*-chlorobromobenzene in 15 cc. of ether and 20 cc. of benzene; yield, 1.7 g. (48%).

Preparation of the Pinacols.—Several pinacols were prepared by interaction of a diketone RCOCOR and a Grignard reagent; most of them were obtained by reduction of an aromatic ketone (a) by zinc and acetic acid; (b) by Mg + MgI_2; (c) photochemically. The general procedure for the first method of reduction consisted in dissolving 10 g. of ketone in 100 cc. of acetic acid and adding 10 g. of zinc dust; during the course of one or two weeks of standing at room temperature, the mixture was stirred occasionally and treated with an additional 10 g. of zinc.

In all cases the pinacols were recrystallized from a mixture of chloroform and alcohol. Most of the pinacols are very soluble in acetone and in chloroform, fairly soluble in alcohol and only slightly soluble in ligroin. In this table there is also shown the transitory color exhibited by the pinacols when they are added to a solution of sodium ethylate in a mixture of ether and benzene; the color is attributed to the intermediate formation of sodium ketyl radicals, R_1R_2CONa.[9]

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[8] Gomberg and Bachmann, THIS JOURNAL, **49**, 236 (1927).

[9] See Bachmann, *ibid.*, **55**, 355 (1933).

Rearrangement of the Pinacols.—Rearrangement was usually attempted by refluxing 2 to 4 g. of the pinacol with a mixture of acetyl chloride, acetic acid and benzene for two to four days. This treatment was found to be ineffective for rearranging 3,3′-dimethoxybenzopinacol, 3,3′-dimethoxy-3″,3‴-dimethylbenzopinacol and 3,3′-dichloro-4″,4‴-diphenylbenzopinacol, and for these pinacols we employed a more powerful reagent.[8] Fifteen to thirty minutes of refluxing with a solution of 0.05 g. of iodine in 15 cc. of acetic acid sufficed for rearranging all pinacols with which it was tried. In order to determine whether the migrations of the groups are independent of the rearranging agent, we have rearranged two pinacols by means of acetyl chloride and also by acetic acid and iodine; in Table IV the results obtained by the two methods are compared.

TABLE IV

EFFECT OF REARRANGING AGENT ON MIGRATION OF GROUPS

sym-Benzopinacol	Migration of	Migration, % AcCl	AcOH-I_2
4,4′-Diethoxy-	Phenetyl	98.7	97.9
	Phenyl	1.3	2.1
3,3′-Dimethoxy-4″,4‴-dimethyl-	*p*-Tolyl	91.3	88.3
	m-Methoxyphenyl	8.7	11.7

As far as these results are concerned, it appears that the course of rearrangement is practically independent of the nature of the rearranging agent. We are planning to investigate the action of several rearranging agents on a large number of pinacols in order to test this point completely.

The mixture of pinacolones was cleaved into triarylmethanes and acids by refluxing for two to four days with a 25% solution of potassium hydroxide in methyl alcohol; in addition one-third by volume of benzene was used to aid in dissolving the pinacolones. The yields of triarylmethanes were within a few per cent. of the theoretical while the amounts of acids were usually greater than 90% of the calculated amount. The extent of migration undergone by each group in the pinacol was determined by analysis of the acid mixtures. In the mixtures containing the alkoxylbenzoic acids, the proportion of these acids was estimated by making a methoxyl or ethoxyl determination, using the method of Vieböck and Schwappach.[10] The proportion of *p*-toluic acid in admixture with *p*-chlorobenzoic acid was determined by extracting the toluic acid with hot water and oxidizing it by potassium permanganate solution to the insoluble terephthalic acid; a number of runs made on synthetic mixtures demonstrated the applicability of the method. The results of the analyses on samples from different runs always checked each other closely.

3-Methoxy-4′,4″-diphenyltriphenylmethane.—This compound was obtained in the form of colorless needles in 57% yield by the scission of the pinacolones produced by rearrangement of *sym*-3,3′-dimethoxy-4″,4‴-diphenylbenzopinacol; m. p. 149–149.5°. The structure of the compound was proved by synthesis. To the lithium derivative obtained by interaction of 7 g. of *p*-bromobiphenyl and 0.42 g. of lithium in 30 cc. of ether was added 25 cc. of benzene and 3 g. of 3-methoxy-4′-phenylbenzophenone. After three hours of refluxing, the mixture was hydrolyzed. The 3-methoxy-4′,4″-diphenyltriphenylcarbinol which was formed was reduced to the corresponding methane by hot formic acid. After being recrystallized three times from chloroform and alcohol and from benzene and ligroin the methane was obtained in clusters of colorless needles, which melted at 148° alone and when mixed with the triarylmethane obtained from the pinacolone. The 3-methoxy-4′,4″-diphenyltriphenylmethane is soluble in acetone, benzene and chloroform and is slightly soluble in alcohol and petroleum ether.

Anal. Calcd. for $C_{32}H_{26}O$: C, 90.1; H, 6.2. Found: C, 89.5; H, 6.3.

4-Chloro-4′,4″-dimethoxytriphenylmethane.—The mixture of triarylmethanes which resulted on scission of the pinacolones from 4,4′-dichloro-4″,4‴-dimethoxybenzopinacol solidified when it was stirred with alcohol; by recrystallization from acetone and alcohol one of the triarylmethanes was obtained in 50% yield as long colorless needles; m. p. 65–66°. The product proved to be identical with 4-chloro-4′,4″-dimethoxytriphenylmethane, which was synthesized by making the carbinol from 4,4′-dimethoxybenzophenone and the Grignard reagent from *p*-chlorobromobenzene, followed by reduction of the triarylcarbinol by zinc and acetic acid.

Anal. Calcd. for $C_{19}H_{13}Cl(OCH_3)_2$: OCH_3, 18.3. Found: OCH_3, 17.8.

3-Chloro-4′,4″-diphenyltriphenylmethane.—The triarylmethane which was obtained by alkali cleavage of the pinacolone from 3,3′-dichloro-4″,4‴-diphenylbenzopinacol proved to be practically pure 3-chloro-4′,4″-diphenyltriphenylmethane, m. p. 144–145°, as was to be expected from the nature of the acid. The triarylmethane was synthesized. A quantitative yield of 3-chloro-4′,4″-diphenyltriphenylcarbinol was obtained by refluxing a mixture of 6.7 g. of 4,4′-diphenylbenzophenone and the Grignard reagent from 7.1 g. of *m*-chloroiodobenzene in 20 cc. of ether and 20 cc. of benzene; the carbinol gives a deep red color with concentrated sulfuric acid. By heating the carbinol with formic acid for twelve hours, 3-chloro-4′,4″-diphenyltriphenylmethane was formed.

Anal. Calcd. for $C_{31}H_{23}Cl$: Cl, 8.2. Found: Cl, 8.1.

Summary

Ten symmetrical aromatic pinacols of the type $R_1R_2C(OH)(HO)CR_2R_1$ have been prepared and subjected to rearrangement to pinacolones. In each instance the percentage migration of each of the two groups has been determined.

It has been shown that it is possible to predict with considerable accuracy the manner in which a mixed symmetrical pinacol will rearrange.

ANN ARBOR, MICHIGAN RECEIVED JUNE 18, 1934

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[10] Vieböck and Schwappach, *Ber.*, **63**, 2818 (1930).