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Summary

1. Methylmercuric iodide is not formed from methyl iodide and mercury on exposure to light until after the appearance of mercurous iodide in the reaction mixture.

2. Finely divided mercury produced by the photochemical decomposition of mercurous iodide enters into reaction readily with methyl iodide to form methylmercuric iodide.

3. The action of mercury with organic iodides to form organomercuric iodides has been extended to benzyl iodide.

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

THE PINACOL-PINACOLIN REARRANGEMENT. THE REARRANGEMENT OF UNSYMMETRICAL AROMATIC PINACOLS

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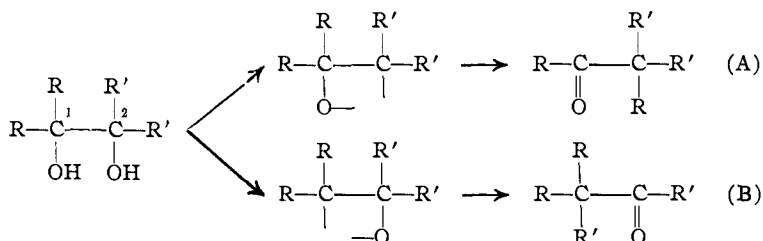
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The rearrangement of symmetrical mixed pinacols of the type $RR'(OH)CC(OH)RR'$ has received considerable attention because the reaction offers an excellent method for determining the relative migration aptitudes of groups. The groups R and R' are in structurally identical positions, and the mode of water elimination from the molecule is therefore immaterial; the principal factor determining the course of the rearrangement is the relative migration aptitudes of the groups. Moreover, it has been shown that in such pinacols each group may be assigned a definite numerical value which represents the migration aptitudes of that group relative to some other group. The most recent series¹ showing the migration aptitudes of a number of groups with respect to the phenyl group taken as unity is the following: anisyl, 70 or more; *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, 0.7; *p*-chlorophenyl, 0.66; *m*-methoxyphenyl, 0.2; *o*-tolyl, *o*-bromophenyl and *o*-chlorophenyl, very small. It has further been demonstrated that by means of these values it is possible to calculate the course of rearrangement of a symmetrical pinacol containing two of these groups.

We have now undertaken an investigation to determine whether the same series holds in the rearrangement of unsymmetrical pinacols of the type $RR(OH)CC(OH)R'R'$. Various investigators have pointed out that in pinacols of this type the nature of the rearrangement depends practi-

¹ Bachmann and Moser, *THIS JOURNAL*, **54**, 1124 (1932).

cally entirely on the possible mode of elimination of water and not at all on the migration aptitudes of the groups. From the following formulation it is apparent that two isomeric pinacolins are possible, the nature of which depends on the particular H and OH that are eliminated.



Meerwein² considered that formation of A is an indication that the OH group attached to C² is held more loosely than the OH of C¹. The strength with which the OH group is held to the carbon atom is considered to be dependent upon the nature of the radicals R and R'; if the radicals attached to a particular carbon atom have large affinity capacities, then the OH will be held proportionately loosely to that carbon atom. Formation of A exclusively is, therefore, an indication that R' has a greater affinity capacity than R. On this basis, the rearrangement offers a method for studying affinity capacities and not migration aptitudes of groups. The view is held by some that the elimination of the hydroxyl group occurs preferentially from that carbon atom to which are attached the groups with the greatest capacity for electron release.³ Whether these views can be applied also to the unsymmetrical aromatic pinacols is not known because no simple aromatic pinacol of this type has been prepared previous to this investigation. Meerwein studied mixed aliphatic-aromatic pinacols and also the unsymmetrical pinacol containing the phenyl and biphenylene groups and recently Bergmann and Schuchardt⁴ rearranged two additional pinacols of this type. In this paper are reported the results obtained by rearranging three unsymmetrical pinacols containing only aryl groups. In each pinacol one carbon atom holds two phenyl groups; to the other carbon atom are attached two anisyl, two *p*-tolyl and two *m*-tolyl groups, respectively, thus offering a comparison of four groups.

In the following table the results obtained previously in the rearrangement of symmetrical pinacols are compared with the results obtained now on unsymmetrical pinacols containing the same groups.

It is immediately apparent that the series representing the relative migration aptitudes of the groups in symmetrical pinacols does not hold for the unsymmetrical pinacols. The series for the latter type of mole-

² Meerwein, *Ann.*, **419**, 121 (1919).

³ "Annual Reports," Vol. 27, 1930, p. 117.

⁴ Bergmann and Schuchardt, *Ann.*, **487**, 285 (1931).

TABLE I
 MIGRATION OF GROUPS

Groups R,R'	RR'(OH)CC(OH)RR' Migration, %	RR(OH)CC(OH)R'R'
<i>p</i> -CH ₃ OC ₆ H ₄	98.6	28
C ₆ H ₅	1.4	72
<i>p</i> -CH ₃ C ₆ H ₄	94	49
C ₆ H ₅	6	51
<i>m</i> -CH ₃ C ₆ H ₄	66	50
C ₆ H ₅	34	50

cule may be represented as follows: phenyl, 1; *m*-tolyl, 1; *p*-tolyl, 0.96; anisyl, 0.39. It is especially striking that the anisyl group, which in the symmetrical pinacol migrates nearly exclusively with respect to the phenyl group, migrates to a lesser extent than the phenyl group when these two groups are in the unsymmetrical molecule. If these results are indications of affinity capacities, then the affinity capacities of the groups are: anisyl, 2.57; *p*-tolyl, 1.04; *m*-tolyl, 1; phenyl, 1. It is evident that the value representing the migration aptitude of a group in a certain type of molecule cannot be applied indiscriminately to that group when situated in a different type of molecule.

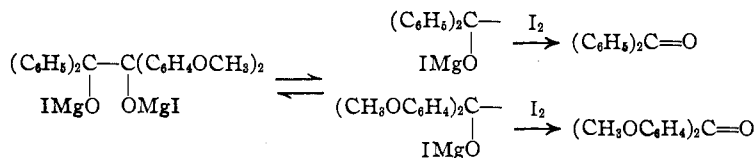
Work is in progress to determine the relative migration aptitudes of a large number of groups in unsymmetrical pinacols. We wish, moreover, to determine whether it is possible to predict the rearrangement of pinacols containing any two given groups when the relative migration aptitude of each group with respect to a third mutual group is known. Thus, from the results given in Table I, one can calculate that the unsymmetrical pinacols, di-*p*-tolyl-dianisylglycol, di-*m*-tolyl-dianisylglycol and di-*p*-tolyl-di-*m*-tolylglycol, will rearrange to pinacolins with migration of the groups in the following ratios: *p*-tolyl, 71%; anisyl, 29%; *m*-tolyl, 72%; anisyl, 28%; *p*-tolyl, 49%; *m*-tolyl, 51%. Experiment will show whether these predictions are justified and it is hoped that the results will throw light upon the question of affinity capacities.

At this time we take the opportunity of pointing out certain facts which were apparently overlooked by Bergmann and Schuchardt⁴ when they criticized adversely our interpretation of the mechanism of the reduction of aromatic ketones to pinacols by the system magnesium and magnesium iodide.⁵ The failure to find benzophenone and benzhydrol on hydrolysis of the reaction mixture does not prove that iodomagnesium ketyl is not initially formed and is not present in small amount. Bergmann and Schuchardt entirely overlooked our formulation of an equilibrium between the iodomagnesium ketyl radicals initially formed and the iodomagnesium pinacolate, $2 R_2COMgI \rightleftharpoons R_2(OMgI)CC(OMgI)R_2$. Obviously, if this equilibrium is nearly entirely in favor of the dimolecular form, then

⁵ Gomberg and Bachmann, *THIS JOURNAL*, **49**, 236 (1927).

only pinacol will be formed on hydrolysis. The situation is analogous to that of diphenyldibiphenyleneethane which in solution dissociates to a very limited extent only into phenylbiphenylene radicals. Bergmann and Schuchardt attribute the color formation in the solution to a small amount of a saturated ketone-magnesium compound, analogous to benzophenone-disodium, $R_2C(ONa)Na$, instead of to the free iodomagnesium ketyl, $R_2\overset{\diagup}{C}OMgI$, which we consider is responsible. In doing so they forget that the solution of pinacolate reacts with iodine and with oxygen at room temperature, that in this reaction the color of the solution is discharged and the ketone is formed; moreover, that even after 90% of the pinacolate has been converted to ketone by this process, the color returns to the solution provided that oxygen and iodine be excluded. They agree with us that the magnesium pinacolate⁶ $R_2C(OMgO)R_2$ is capable of dissociation into colored radicals but, curiously enough, they seem to deny this property to the corresponding iodomagnesium pinacolate, $R_2(OMgI)CC(OMgI)R_2$. Finally, Bergmann and Schuchardt have overlooked the fact that by the action of a Grignard reagent such as methylmagnesium iodide on pure pinacol, there is obtained the equilibrium system, iodomagnesium pinacolate \rightleftharpoons iodomagnesium ketyl, which exhibits the same color and the same reactions as the system obtained by reduction of the ketone by the binary mixture. It is evident that the reaction between pinacol and Grignard reagent cannot possibly give rise to a saturated ketone-magnesium compound analogous to the ketone-disodium compound.

In this connection it was of interest to see whether the pinacolate of an unsymmetrical pinacol would behave like the symmetrical pinacolates. Accordingly, the pinacolate of *as*-diphenyldianisylglycol was made by adding ethylmagnesium iodide to a solution of the pinacol. The pinacolate solution absorbed iodine and the pinacolate was converted to a mixture of benzophenone and 4,4'-dimethoxybenzophenone. The behavior of the pinacolate is best explained by the following formulations



The pinacolate obtained from *as*-diphenyldi-*m*-tolylglycol behaved in a similar fashion. It remains to be seen whether it is possible for two symmetrical pinacols, $RR(OMgI)CC(OMgI)RR$ and $R'R'(OMgI)CC-$

⁶ Bergmann and Schuchardt confirm the results we obtained on the composition of the reduction product; by indirect means they showed the presence of magnesium pinacolate, a result that we had obtained by direct analysis.

(OMgI)R'R', to be formed by recombination of the radicals which are formed by dissociation of the pinacolate of an unsymmetrical pinacol, RR(OMgI)CC(OMgI)R'R'.

Experimental

Preparation of the Pinacols.—Acree⁷ isolated benzopinacol from the reaction between methyl benzilate and an excess of phenylmagnesium bromide. Meerwein² attempted the preparation of *as*-diphenylditolylglycol and *as*-diphenyldianisylglycol by a similar reaction but he reported that the hydroxy ketone and not the glycol resulted. We have employed Acree's method with modifications and were able to synthesize several unsymmetrical pinacols, including those which Meerwein wished to make, although in two cases the hydroxy ketone and not the glycol was isolated.

The general procedure consists in adding a solution of 0.05 g. mole (12.1 g.) of methyl benzilate in 50 cc. of benzene to the Grignard reagent which has been prepared from 0.2 g. mole of the appropriate aryl halide (*p*-bromotoluene, bromoanisole, etc.). After being refluxed for twelve hours the mixture is hydrolyzed with cold ammonium chloride solution. The ether-benzene solution is filtered and evaporated. The crude pinacol is digested with ligroin or alcohol in order to remove oily impurities and the pinacol is filtered off and recrystallized.

Rearrangement of the Pinacols.—The pinacols were rearranged according to the general procedure described in a preceding paper.¹ In the case of the diphenylditolylglycols the rearrangement did not seem to be complete; in these cases the reaction was completed by heating the partially rearranged material with acetic acid and iodine.⁸ The mixture of pinacolins was cleaved with potassium hydroxide in the customary manner, RRRCCOR + KOH \longrightarrow RRRCH + KOOCR; from the nature of the mixture of acids so obtained it is possible to calculate the extent of migration undergone by each group. Unlike the symmetrical pinacols, the acid which is isolated corresponds to the group which has migrated; thus, the amount of benzoic acid in the mixture indicates the extent of migration of the phenyl group. It is noteworthy how closely the results of several rearrangements agree with one another.

as-Diphenyldi-*p*-tolylglycol,⁸ (C₆H₅)₂(OH)CC(OH)(C₆H₄CH₃)₂.—The pinacol was recrystallized by adding alcohol to a hot acetone solution of the compound; the pinacol crystallized in colorless needles; yield, 54%; m. p. 167–168° with decomposition. The pinacol is not very soluble in hot alcohol but it dissolves readily in hot acetone and in hot benzene.

Anal. Calcd. for C₂₈H₂₆O₂: C, 85.2; H, 6.6. Found: C, 84.9; H, 6.6.

The mixture of benzoic acid and *p*-toluic acid which was obtained by cleavage of the pinacolins was analyzed by oxidizing the *p*-toluic acid to terephthalic acid¹ which in virtue of its insolubility in water is easily separated from benzoic acid. At the same time a control oxidation was carried out on a synthetic mixture of the two acids of approximately the same composition. The mixtures from two rearrangements were found to have the following compositions by weight: benzoic acid, 47.9%, 47.7%; *p*-toluic acid, 52.1%, 52.3%; average composition by moles: benzoic acid, 50.7%; *p*-toluic acid, 49.3%. Yield of acids: 93%, 94% of the theoretical amount based on the pinacol employed; yield of triarylmethanes: 97%, 98%.

⁷ Acree, *Ber.*, **37**, 2761 (1904).

⁸ According to Tiffeneau and Lévy, *Bull. soc. chim.*, [4] **49**, 1650 (1931), Erdmann [Thesis, Rostock, 1910] prepared diphenyldi-*p*-tolylglycol but did not study its rearrangement. We did not have Erdmann's thesis at hand and have been unable to find any reference in the literature to the pinacol.

From the mixture of pinacolins which is formed on rearrangement of the pinacol it was possible to isolate one of them in a pure state. Three and one-half grams of pinacol was heated with 10 cc. of acetic acid and 0.5 g. of iodine for ten minutes; the solution was cooled and decolorized with sulfur dioxide. On standing for several days, the solution deposited 1.1 g. of benzoildi-*p*-tolylphenylmethane, $C_6H_5CO(C_6H_4CH_3)_2C_6H_5$. After recrystallization from acetic acid, the compound melted at 133–135° and was found to be identical with the compound of known structure, which is formed on rearrangement of symmetrical diphenyldi-*p*-tolylglycol. The isomeric pinacolin which was obtained from the mother liquors was difficult to obtain in a pure state.

***as*-Diphenyldi-*m*-tolylglycol**, $(C_6H_5)_2(OH)CC(OH)(C_6H_4CH_3)_2$.—By recrystallization from a mixture of acetone and alcohol the pinacol was obtained in the form of needle-like prisms; yield, 56%; m. p. 156–158° with decomposition. The pinacol is very soluble in hot benzene and in hot acetone, but it is not very soluble in alcohol.

Anal. Calcd. for $C_{28}H_{26}O_2$: C, 85.2; H, 6.6. Found: C, 85.1; H, 6.6.

The amount of *m*-toluic acid present in the mixture of acids was determined by oxidizing the toluic acid to isophthalic acid which, being little soluble in water, can be readily separated from benzoic acid. Composition by weight of acid mixture (two rearrangements): benzoic acid, 47%, 48%; *m*-toluic acid, 53%, 52%; average composition by moles: benzoic acid, 50.2%; *m*-toluic acid, 49.8%; yield of acids: 90%, 91%; yield of triarylmethanes: 98%, 100%.

***as*-Diphenyldianisylglycol**, $(C_6H_5)_2(OH)CC(OH)(C_6H_4OCH_3)_2$.—Recrystallization of the crude pinacol from a mixture of acetone and alcohol gave colorless needles; yield, 60%; m. p. 166–168°. The pinacol is not very soluble in hot alcohol but it dissolves readily in hot acetone and in hot benzene.

Anal. Calcd. for $C_{28}H_{26}O_4$: C, 78.8; H, 6.1. Found: C, 78.8; H, 6.1.

The mixture of benzoic acid and anisic acid was analyzed by making a methoxy determination. Composition of acid mixture by weight: benzoic acid, 67.1%, 66.8%; anisic acid, 32.9%, 33.1%; average composition by moles: benzoic acid, 71.6%; anisic acid, 28.4%. Yield of acids: 92%, 97%; yield of triarylmethanes: 102%, 100%. By recrystallization of the mixture of triarylmethanes from alcohol, pure phenyldianisylmethane (m. p. 100°) was isolated.

Diphenyl-*o*-toluylcarbinol, $(C_6H_5)_2(OH)CCOC_6H_4CH_3$.—The action of *o*-tolylmagnesium bromide on methyl benzilate gave an oil from which a small amount of crystals was isolated. These crystals proved to be not the pinacol but the hydroxy ketone, diphenyl-*o*-toluylcarbinol, resulting by the addition of only one molecule of Grignard reagent to the ester group. Recrystallization from acetone and alcohol gave colorless needles; m. p. 116–117°. The compound was split quantitatively into benzhydrol and *o*-toluic acid when it was heated with three parts of a 25% solution of potassium hydroxide in methyl alcohol⁹ for five minutes. The carbinol gives an orange-red color with concentrated sulfuric acid.

Anal. Calcd. for $C_{21}H_{18}O_2$: C, 83.4; H, 6.1. Found: C, 83.5; H, 6.1.

Diphenyl- α -naphthoylcarbinol, $(C_6H_5)_2(OH)CCOC_{10}H_7$.—The reaction between methyl benzilate and α -naphthylmagnesium bromide gave an oil and several grams of crystals of diphenyl- α -naphthoylcarbinol. Recrystallization from a mixture of acetone and alcohol gave colorless needles; m. p. 156–157°. On being heated with a methyl alcohol solution of potassium hydroxide the carbinol was cleaved quantitatively into benzhydrol and α -naphthoic acid. The carbinol gives a dark brown color with sulfuric acid.

Anal. Calcd. for $C_{24}H_{18}O_2$: C, 85.1; H, 5.4. Found: C, 84.7; H, 5.3.

⁹ Acree, *Am. Chem. J.*, **29**, 597 (1903).

It is planned to prepare the desired *as*-diphenyl-*o*-tolylglycol and *as*-diphenyldi- α -naphthylglycol by the action of phenylmagnesium bromide on the esters of *o*-tolilic acid and α -naphthilic acid, respectively.

Reaction between Iodomagnesium-diphenyldianisylglycolate and Iodine.—Two grams of *as*-diphenyldianisylglycol was added to a solution of ethylmagnesium iodide in a mixture of ether and benzene; a red color developed but quickly disappeared. The solution absorbed iodine, slowly at room temperature, much more rapidly when heated. The solution was finally warmed with iodine for several hours, then cooled and hydrolyzed. The ether-benzene solution yielded a mixture of benzophenone and 4,4'-dimethoxybenzophenone. The benzophenone was extracted by warming the mixture of ketones with 10 cc. of petroleum ether and filtering the hot mixture. The residual dimethoxybenzophenone after recrystallization from benzene and ligroin melted at 142–144°; yield, 1.0 g. or 87%.

Summary

Three unsymmetrical aromatic pinacols, *as*-diphenyldi-*p*-tolylglycol, *as*-diphenyldi-*m*-tolylglycol and *as*-diphenyldianisylglycol, have been synthesized and rearranged to pinacolins.

These pinacols rearrange to pinacolins with migration of the groups in the following ratios: *p*-tolyl, 49%, phenyl, 51%; *m*-tolyl, 50%, phenyl, 50%; anisyl, 28%, phenyl, 72%.

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NOTE

Note on the Preparation of Mercury Dibenzyl

BY J. LEWIS MAYNARD

The preparation of this substance in a pure condition and in good yields has heretofore presented certain difficulties. An attempt to prepare it by a reaction of general application to this type of compound failed to yield the desired substance. Benzyl bromide and sodium amalgam do not react to form mercury dibenzyl.¹ It was first prepared by the Grignard reaction between benzylmagnesium chloride and mercuric chloride.² The product was slightly impure, as was shown by the melting point of 104°, seven degrees below the true melting point. No yield was given, and the substance was said to possess a characteristic sweet odor. This is not shown by the pure substance.

Other investigators have also used the Grignard reaction to prepare mercury dibenzyl, but the yields either have not been given, or have not

¹ Wurtz, *Compt. rend.*, **68**, 1300 (1869); Dreher and Otto, *Ann.*, **154**, 93 (1870). Cf. Campisi, *Compt. rend.*, **61**, 861 (1865). The product obtained by the latter melted over 90° higher than pure (C₆H₅CH₂)₂Hg.

² Pope and Gibson, *J. Chem. Soc.*, **101**, 735 (1912).