The total materials extracted by the ether and by the water were determined as well as the amount of residue remaining. The quantity of material extracted by the combined salt, alcohol and alkali extractions was calculated by difference.

The similarity between the two grass pollens and between the two ragweed pollens is very marked. The grass pollens swelled greatly in alkali while the ragweed pollens did not. The ragweed pollens contain much more ether-soluble material, but only approximately half as much material extractable by water.

The differences in nitrogen content in the similar fractions of the different pollens do not appear to be significant. About half of the nitrogen was not extractable by the solvents used.

The results on the water extracts indicate that most of the nitrogen extracted by this solvent is non-protein. It also appears that the water extract contains globulin.

INDIANAPOLIS, INDIANA

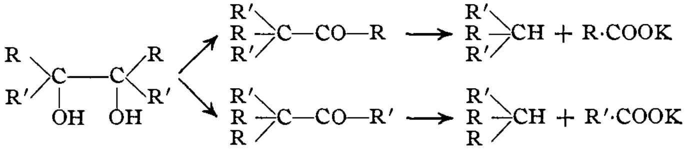
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE EFFECT OF SUBSTITUENTS UPON THE REARRANGEMENT OF BENZOPINACOL

BY JOHN C. BAILAR, JR.

RECEIVED APRIL 30, 1930 PUBLISHED SEPTEMBER 5, 1930

The relative migratory tendencies of organic radicals have often been determined by means of molecular rearrangements. Any rearrangement in which two groups occupy identical positions and are equally free to move might theoretically be used for this purpose, but if the two groups are nearly equal in migratory tendency, each will migrate to some extent, and a mixture of two isomeric products will be formed. The separation of these, or a determination of the relative amounts in which they are present, is often difficult. In the case of the pinacol rearrangement, however, each of the two pinacolones which are formed may be split by the action of alcoholic potassium hydroxide into a hydrocarbon and the potassium salt of an acid. These acids are often readily separated.



Thus Montagne has determined the relative migratory tendencies of the *p*-chlorophenyl and phenyl groups[1] and the *p*-bromophenyl and

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[1] Montagne, *Rec. trav. chim.*, **26**, 253 (1907).

phenyl groups,[2] separating the substituted and unsubstituted acids by the difference in their solubilities. In like manner Gomberg and Bachmann[3] compared the *p*-biphenyl and phenyl groups, and Gomberg and Bailar[4] have compared the *p*-biphenyl group with the *m*- and *p*-bromophenyl groups, separating the acids by the difference in the solubility of the barium salts.

But in many cases a quantitative separation of the acids or their salts is a long and tedious process. The comparisons reported in this article have been made possible by the use of a method which depends upon the determination of the equivalent weight of the mixture of the acids formed from the pinacolones. Knowing this, and the equivalent weight of the two acids which might possibly be present, it is easy to calculate the percentage composition of the mixture, and from this the relative migratory tendencies of the two groups. The equivalent weight of the mixture is determined by titration of a weighed sample with a standard base. The method is not an extremely accurate one, but repeated and careful experiments have shown that the composition of the mixture can be calculated within 5%, even when the two acids are as similar as benzoic and toluic acids.

Experimental

During the course of this investigation ten symmetrically substituted benzopinacols have been subjected to rearrangement. None of these pinacols has been described in the literature. Table I gives the formulas, melting points and analytical data for these, and also ratios indicating the comparative migratory tendencies of the various groups.

The 4,4′-dimethoxy-di-α-naphthyl pinacol was prepared by the action of α-naphthylmagnesium bromide upon anisil; the *sym.*-2,2′- and 3,3′-dimethoxybenzopinacols by reduction of the corresponding ketones by zinc and acetic acid. In the course of preparation of 3-methoxybenzophenone two compounds not previously described were obtained. 3-Methoxybenzoic acid was converted through the chloride into the amide, and thus into the cyanide. This, by treatment with phenylmagnesium bromide, gave the ketone in good yield.

Amide.—White crystals melting at 130°. *Anal.* Calcd. for $C_8H_9O_2N$: C, 63.54; H, 6.00. Found: C, 63.79; H, 6.11.

Cyanide.—Colorless liquid boiling at 140° at 34 mm. pressure. *Anal.* Calcd. for C_8H_7ON: C, 72.14; H, 5.30. Found: C, 71.97; H, 5.15.

All of the other pinacols were prepared from the corresponding ketones by the method of Gomberg and Bachmann.[3] In every case the yield of crude pinacol was practically quantitative; in some cases large losses were incurred during the process of purification. Bachmann and Shankland have previously encountered this difficulty.[5]

Two of the ketones used were not known previously. 4-Isopropylbenzophenone

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[2] Montagne, *Rec. trav. chim.*, **29**, 154 (1910).

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

[4] Gomberg and Bailar, *ibid.*, **51**, 2236 (1929).

[5] Bachmann and Shankland, *ibid.*, **51**, 306 (1929).

Table I

Constants and Analytical Data

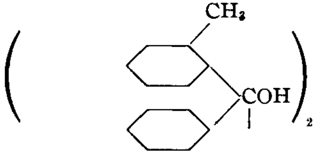
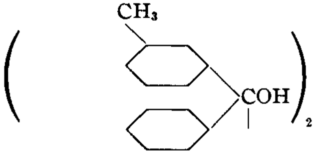
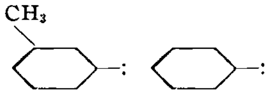
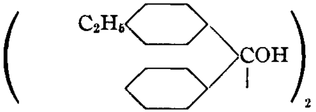
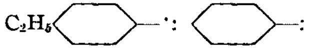
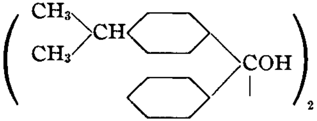
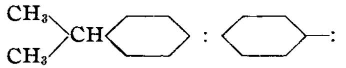
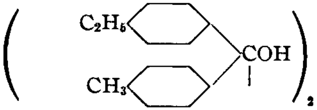
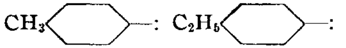
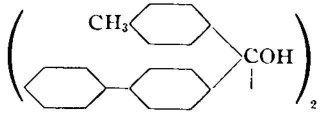
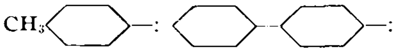
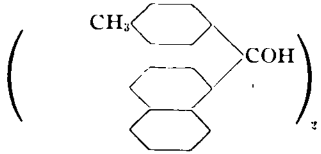
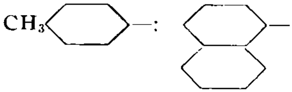
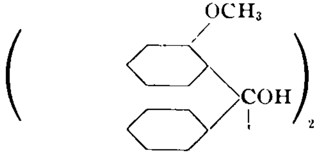
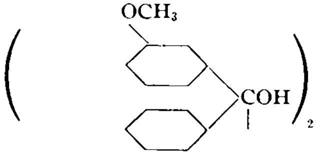
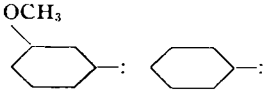
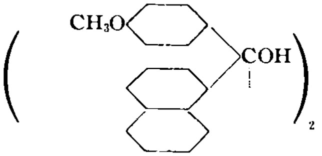
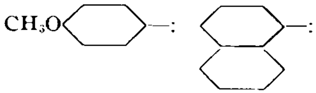
Formula	M. p., °C.	Calcd.	Found	Ratio of migratory tendencies
	156	C, 85.23 H, 6.65	85.09 6.51	No rearrangement
	147–148	C, 85.23 H, 6.65	85.18 6.93	 : : 0.6 : 1
	162–163	C, 85.25 H, 7.16	85.28 6.93	 : : 5 : 1
	161–162	C, 85.28 H, 7.61	85.35 7.41	 : : 9 : 1
	155–156	C, 85.28 H, 7.61	85.02 7.33	 : : 3 : 1

TABLE I (*Concluded*)

Formula	M. p., °C.	Calcd.	Found	Ratio of migratory tendencies
	175–176	C, 87.87 H, 6.28	87.94 6.11	 : : 1 : 1
	150	C, 87.41 H, 6.12	87.60 5.85	 : : 1 : 1.14
	168–169	C, 78.83 H, 6.15	78.89 5.98	No rearrangement
	139–141	C, 78.83 H, 6.15	78.54 6.19	 : : 0.2 : 1
	143–144	C, 82.09 H, 5.75	81.91 5.61	 : : 2 : 1

was obtained by the reaction of benzoyl chloride and isopropylbenzene; yield, 75%. The best yield is obtained when a large excess of isopropylbenzene is used. The ketone is a colorless liquid which does not crystallize at −10°; b. p. 197° at 10 mm.

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.66; H, 7.19. Found: C, 85.44; H, 7.15.

4-Methyl-4′-ethylbenzophenone resulted from the reaction of toluyl chloride and ethylbenzene; yield, 70%. The ketone did not crystallize; b. p. 215° at 10 mm.

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.66; H, 7.19. Found: C, 85.49; H, 7.05.

The determination of the migratory tendencies was made as follows. A 3-g. sample of pure pinacol was subjected to rearrangement by boiling with 30 cc. of glacial acetic acid and a small crystal of iodine for one hour. The solution was poured into 400 cc. of water containing a pinch of sodium bisulfite to remove the iodine. The white precipitate of pinacolone was separated from the liquid by filtration, washed with water and allowed to dry, after which it was boiled with 1 g. of potassium hydroxide in 50 cc. of absolute alcohol for twelve hours. (Two or three hours' boiling suffices to split some pinacolones, but not all of them.) Sometimes the solution turned brown during this boiling; in such cases, the results of the experiments were never concordant, and were discarded. The alcoholic solution was poured into water and evaporated until the precipitate had coagulated. This was then filtered off and the filtrate, which contained the potassium salts of the acids, was extracted with ether in order to remove any remaining traces of foreign organic matter. Upon acidification of the solution, the acids precipitated, and were extracted with ether. The extract was dried over anhydrous sodium sulfate, filtered and allowed to evaporate. The residue was weighed and after being dissolved in alcohol, was titrated with standard sodium hydroxide. The results obtained in the three experiments which were carried out with 4,4′-di-isopropylbenzopinacol are shown in Table II. The average of the three values obtained for the ratio of the migratory tendencies of the substituted and unsubstituted groups is 8.9:1. In Table I this is recorded as 9:1; similarly in other cases, realizing that the method is not one of extreme accuracy, we have taken approximate, simple ratios. The approximation did not require as great a change in any other cases as in this one.

TABLE II

EXPERIMENTAL DATA

	Weight of mixed acids	Cc. of 0.1852 *N* NaOH	Equivalent weight of mixture	Weight percentage of benzoic acid	Mole percentage of benzoic acid	Migratory tendency
1	0.6024	25.22	128.99	87.75	90.34	9.3:1
2	.5948	25.16	127.64	86.67	89.74	8.7:1
3	.4590	19.42	127.64	86.67	89.74	8.7:1

In the case of 4,4′-di-isopropylbenzopinacol one of the pinacolones was formed in so much greater quantity than the other that separation of the two was easy. Three recrystallizations from glacial acetic acid gave pure benzoyl-4,4′-di-isopropyltriphenylmethane; m. p. 140°.

Anal. Calcd. for $C_{32}H_{32}O$: C, 88.52; H, 7.67. Found: C, 88.72; H, 7.47.

This pinacolone, heated with alcoholic potassium hydroxide, gave a quantitative yield of 4,4′-di-isopropyltriphenylmethane. This hydrocarbon resisted all attempts at crystallization. In an ice–salt mixture it solidified to a glassy mass.

Anal. Calcd. for $C_{25}H_{28}$: C, 91.40; H, 8.60. Found: C, 91.61; H, 8.77.

Two of the pinacols—those in which the methyl and methoxy groups occupy the ortho-positions—did not rearrange upon boiling for one hour with glacial acetic acid and iodine. Even four hours' boiling had no effect. Heating for two hours with glacial acetic acid and acetyl chloride (a method often used to effect the rearrangement of pinacols) produced no change—longer heating decomposed the pinacols to a sticky mass of unidentifiable products.

Discussion

Thorner and Acree[6] have reported that in the rearrangement of *sym.*-4,4'-dimethylbenzopinacol only the substituted group moves. This indicates that the *p*-tolyl group has such a large migratory tendency in comparison with that of the phenyl group that no definite comparison can be made between the two. It should be possible to assign a definite value to the migratory tendency of the *p*-tolyl group by comparing it with some other group of large, but known, migratory tendency. Such is the *p*-biphenyl group, which Gomberg and Bachmann[3] have shown to have a migratory tendency 12.5 times as great as that of the phenyl group. The rearrangement of symmetrical 4,4',4'',4'''-dimethyldiphenylbenzopinacol shows the *p*-tolyl and *p*-biphenyl groups to have approximately equal migratory tendencies (Table I). In making this determination we not only determined the equivalent weight of the mixed acids, as outlined above, but we separated the two acids by dissolving the toluic acid out of the mixture with boiling water, in which *p*-phenylbenzoic acid is insoluble. The two methods gave the same result. The relation between the migratory tendencies of the *p*-tolyl group and the phenyl group has been confirmed by another indirect comparison. The substitution of an ethyl group increases the migratory tendency of the phenyl group five-fold; the rearrangement of symmetrical 4,4',4'',4'''-dimethyldiethylbenzopinacol shows that a methyl group in the para-position has three times the effect of an ethyl group. From this it may be inferred that the *p*-tolyl radical has a migratory tendency approximately fifteen times as great as the phenyl. A direct comparison of the two is difficult because of the great similarity in their properties and equivalent weights.

The substitution of a methyl radical in the meta-position decreases the migratory tendency of the phenyl radical somewhat; if the substitution is made in the ortho-position, the migratory tendency becomes very small indeed. Not only does the substituted group fail to migrate—it prevents the migration of the unsubstituted group as well. Such a result was not wholly unexpected—Koopal[7] has reported that benzopinacol in which a chlorine or bromine atom has been substituted in the ortho-position rearranges only very slowly—when rearrangement does take place, it is due entirely to the migration of the unsubstituted group. According to Lagrave[8] this inhibition of the rearrangement can be ex-

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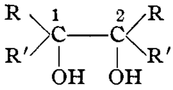
[6] Thorner, *Ber.*, **9**, 482, 1738 (1876); *Ann.*, **189**, 110 (1877); Acree, *Am. Chem. J.*, **33**, 190 (1905).

[7] Koopal, *Rec. trav. chim.*, **34**, 134 (1915).

[8] Lagrave, *Ann. chim.*, [10] **8**, 363 (1927).



plained in the following way. Upon rearrangement of a pinacol, one or the other of the radicals attached to one of the central carbon atoms (C 2) migrates to the other central carbon atom (C 1), but if C 1 is already holding groups of large affinity capacity, it will be unable to accept another group. Such is the case here; the *o*-tolyl group absorbs so much of the energy of C 1 that very little is left to attract another group from C 2. Hence no rearrangement takes place.

Tiffeneau and Orekhoff[9] have shown that the *p*-anisyl radical migrates exclusively in the rearrangement of 4,4′-dimethoxybenzopinacol. As is shown in Table I, the *m*-anisyl radical has but one-fifth of the migratory tendency of the unsubstituted phenyl group, and the presence of the methoxy group in the ortho position prevents any rearrangement. The *p*-anisyl group has twice the migratory tendency of the α-naphthyl group, which in turn is somewhat larger than that of the *p*-tolyl group. The ratio of the migratory tendencies of the *p*-anisyl and phenyl groups is, therefore, in the neighborhood of 40:1.

It will be noticed that the *p*-anisyl group has a much greater tendency to migrate than the *m*-anisyl, which, however, is still more prone to migrate than the *o*-anisyl. The same is true, though less marked, if the substituent is the methyl radical instead of the methoxy. It is apparently true also when the substituent is either a chlorine or a bromine atom.[1,7]

The *p*-isopropylphenyl group has nine times the migratory tendency of the unsubstituted phenyl radical. Thus the effect of the *p*-isopropyl group is not as large as that of the *p*-methyl, but is much larger than that of the *p*-ethyl. Whether this peculiarity be due to the branching of the chain, or to some other factor, cannot be stated without further experimentation.

From the results of this investigation and those of previous workers, the migratory tendencies of various aromatic radicals may be arranged in the following series: (the migratory tendency of the phenyl radical has been chosen as unity) *p*-anisyl, about 40; α-naphthyl, about 18; *p*-tolyl, 12–15; *p*-biphenyl,[2] 12.5; *p*-isopropylphenyl, 9; *p*-ethylphenyl, 5; *p*-fluorophenyl,[7] 1.86; *p*-iodophenyl,[7] 1; phenyl, 1; *p*-bromophenyl,[1] 0.75; *p*-chlorophenyl,[1] 0.66; *m*-tolyl, 0.6; *m*-anisyl, 0.2; *o*- and *m*-bromophenyl, *o*- and *m*-chlorophenyl[7]; *o*-tolyl, *o*-anisyl, very small. It is known also that the β-naphthyl group has a much larger migratory tendency than the phenyl group,[5] but just how much larger has not been determined.

Summary

1. Ten aromatic pinacols have been subjected to rearrangement, and the relative effect of various substituents in the phenyl group has been noted.

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[9] Tiffeneau and Orekhoff, *Bull. soc. chim.*, **37**, 430 (1925).

2. The various groups have been arranged in order of their migratory tendencies. Definite values have been assigned when possible.

3. *m*-Methoxy cyanobenzene, *m*-methoxybenzamide, benzoyl-4,4'-di-isopropyltriphenylmethane, and 4,4'-di-isopropyltriphenylmethane have been described, in addition to the ten pinacols, none of which has previously been reported in the literature.

URBANA, ILLINOIS

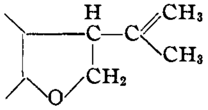
[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

ROTENONE. VIII. ISOMERIC HYDROXY ACIDS AND THEIR RELATION TO DEHYDROROTENONE

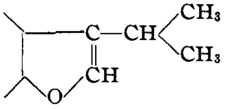
BY F. B. LAFORGE AND L. E. SMITH

RECEIVED MAY 14, 1930 PUBLISHED SEPTEMBER 5, 1930

Rotenone is converted by a number of oxidizing agents into dehydrorotenone, with the loss of two hydrogen atoms. In a recent article, Butenandt has shown that a double bond is formed in this process.[1] Although this new double bond cannot be reduced by catalytic hydrogenation, its presence in dehydrorotenone can be demonstrated by the reaction of Diels,[2] which involves a condensation of a conjugated system with maleic anhydride. It has also been demonstrated that the optically active tubaic acid obtained by cleavage of rotenone with alcoholic potassium hydroxide is converted into inactive rotenic acid under the same conditions by which rotenone is converted into isorotenone and that isorotenone yields rotenic acid by cleavage with alcoholic potassium hydroxide.[1,3] It follows from these facts with a fair degree of certainty that the isomerism between rotenone and isorotenone is due to the same cause as the isomerism between tubaic and rotenic acids. The change involved may be illustrated by the tentative formulas I and II. In these formulas the positions of attachment of the side chain, as well as that of the hydroxyl and carboxyl groups not shown in the figures are as yet undetermined.[4]



I. Tubaic acid



II. Rotenic acid

Since an asymmetric center disappears in this process and since isorotenone is optically active, Butenandt infers that this compound still contains one or more asymmetric carbon atoms in the other half of the molecule, about which little was known to him at the time.

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[1] Butenandt and Hildebrandt, *Ann.*, 477, 245 (1929).

[2] Diels and Adler, *ibid.*, **460**, 102 (1928).

[3] Takei, *Ber.*, **63**, 508 (1930); Haller and LaForge, THIS JOURNAL, **52**, 2480 (1930).

[4] Haller and LaForge, *ibid.*, **52**, 3207 (1930).