

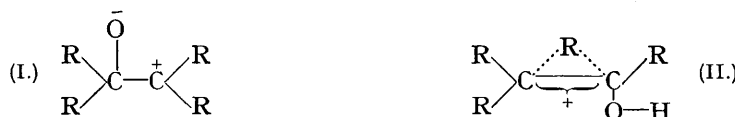
## 82. The Pinacol-Pinacolone Rearrangement of Phenyl-substituted Benzopinacols.

By H. H. HATT, A. PILGRIM, and (MISS) E. F. M. STEPHENSON.

The preparation and rearrangement of *s*.-di-*o*-phenylbenzopinacol and of *s*.-di-*m*-phenylbenzopinacol are described and the rearrangement of *s*.-di-*p*-phenylbenzopinacol has been re-examined. The migratory aptitudes of *o*-, *m*-, and *p*-diphenyl groups relative to the phenyl group have been determined and are discussed. The values of the migratory aptitudes are influenced by the nature of the agent used to rearrange the pinacols. For these values to be comparable, the rearrangement must proceed quantitatively. The suitability of various rearranging agents is considered. Two isomeric hydrated forms of *s*.-di-*o*-phenylbenzopinacol have been isolated. *o*-, *m*-, and *p*-Phenylbenzophenones have been submitted to alkaline fission and cleavage figures for these ketones are recorded.

THE extensive investigations that have been made of rearrangements of tetra-arylpinacols have dealt little with the migration of polynuclear radicals. The  $\alpha$ - and the  $\beta$ -naphthyl group have been compared with the phenyl group in symmetrical tetra-arylpinacols, but the results are not conclusive. The experiments of Bachmann and Shankland (*J. Amer. Chem. Soc.*, 1929, **51**, 306) and of Bergmann and Schuchardt (*Annalen*, 1931, **487**, 225) show that both naphthyl groups migrate much more readily than the phenyl group and therefore possess large migratory aptitudes. The more exact information given by Bailar (*J. Amer. Chem. Soc.*, 1930, **52**, 3596) assigns to  $\alpha$ -naphthyl a migratory aptitude of 35—250 ( $\text{Ph} = 1$ ) through comparison with *p*-anisyl, and of 14—17 through comparison with *p*-tolyl. An exact migratory aptitude for  $\beta$ -naphthyl is not available. Migita (*Bull. Chem. Soc. Japan*, 1932, **7**, 377, 382) estimates it to be much less than that of *p*-anisyl and a little greater than that of *p*-diphenyl. This might mean a value of 5—6, but Migita's methods for the determination of migratory aptitudes are unsatisfactory. It is reasonable to conclude that the  $\alpha$ - and the  $\beta$ -naphthyl group have large migratory aptitudes and that in spite of greater steric opposition the  $\alpha$ -naphthyl group has considerably the larger migratory aptitude.

Shopee pointed out in 1929 (see Baker, "Tautomerism," 1934, 308) that in the pinacol-pinacolone rearrangement, after the formation of the supposed intermediate (I), the subsequent migration of the aryl group, if the order of migratory aptitudes for aryl groups is to be explained, must take place, not, as was usually postulated, as an anion, but as a cation, with simultaneous migration of the electron pair it has shared. The migration appears to take place intramolecularly, and Ingold has re-interpreted the facts of the rearrangement by postulating as intermediate the mesomeric cation (II) (*Ann. Reports*, 1939, **36**, 197).



The probability that the migrating group does not attain a free ionic condition, but migrates within the sphere of influence of the remainder of the molecule, suggests that the migratory aptitude would be increased by factors which enable the group to tolerate any partial polarisation of its covalent bond of attachment. With polynuclear radicals the order of increasing migratory aptitude ought then to parallel the order in which they confer increasing stability upon triarylmethyl radicals, given by Burton and Ingold (*Proc. Leeds Phil. Soc.*, 1929, **1**, 421; see also Ingold, *Trans. Faraday Soc.*, 1934, **30**, 52):  $\alpha$ -naphthyl >  $\beta$ -naphthyl > *p*-diphenyl > *m*-diphenyl > phenyl. The prediction of Burton and Ingold (*loc. cit.*) concerning triarylmethyl stability, *p*-diphenyl > *m*-diphenyl > phenyl, has been experimentally verified by Marvel, Mueller, and Ginsberg (*J. Amer. Chem.*

*Soc.*, 1939, **61**, 78, 2008).\* We have found the following migratory aptitudes in the pinacol-pinacolone rearrangement: *p*-diphenyl, 3·7; *m*-diphenyl, 0·4; phenyl, 1·0, leading to the order:  $\alpha$ -naphthyl >  $\beta$ -naphthyl > *p*-diphenyl > *m*-diphenyl, in agreement with the above suggestion. That the *m*-diphenyl group migrates less readily than phenyl may be due to a factor being involved in determining the migratory aptitude of a group which cannot operate in deciding the effect of the group on triarylmethyl stability, namely, steric opposition to migration. Greater steric opposition to *m*-diphenyl than to phenyl migration would account for the lower migratory aptitude of the first group.

Previously, it has been suggested (Beale and Hatt, *J. Amer. Chem. Soc.*, 1932, **54**, 2405) that the migratory aptitudes of *o*-substituted groups may be regarded as derived from those of the isomeric *p*-substituted groups by applying a correction for the *o*-effect. The latter, being largely steric in nature and hindering migration, necessitates that *o*-substituted groups possess small migratory aptitudes. The experimental values are so small that, with the exception of *o*-anisyl, they are all zero relative to phenyl. In agreement with this view it is now found that the phenyl group alone migrates in the rearrangement of *s*-di-*o*-phenylbenzopinacol. Models of this pinacol show that steric opposition to rearrangement should be especially pronounced. That rearrangement is even possible can be regarded as additional evidence of its intramolecular nature, for the phenyl group, when once removed from the molecule as an ion, could re-enter only with difficulty and some smaller ion would be expected to enter in its place. This pinacol is difficult to rearrange and the agents that have previously been described in the literature were found ineffective. Hydron is usually the effective agent in these rearrangements and for this reason it seemed that perchloric acid in acetic acid solution was most likely to prove successful (compare Conant and Hall, *J. Amer. Chem. Soc.*, 1927, **49**, 3047). The reagent rapidly brought about complete rearrangement in this case, and in other pinacol-pinacolone changes examined, because of the rapidity of rearrangement, it seemed the most suitable agent to employ.

So that the migratory aptitudes obtained with perchloric acid should be comparable with the results obtained with other agents, a comparison of agents has been made, *s*-di-*p*-phenylbenzopinacol being used as substrate. The results (Table I) show that the extent to which *p*-diphenyl and phenyl groups migrate is independent of the agent used except in the case of acetyl chloride in acetic acid-benzene solution. The apparently increased migration of the phenyl group in this case has a simple explanation. Rearrangement with this reagent takes place slowly [Gomberg and Bachmann (*J. Amer. Chem. Soc.*, 1927, **49**, 236) found it necessary to reflux with it for 12 hours, and Bachmann and Moser (*ibid.*, 1932, **54**, 1124) in some cases refluxed the mixture for 60 hours] and permits an appreciable amount of thermal dismutation (compare Bergmann and Schuchardt, *Annalen*, *loc. cit.*, p. 257). The ketone produced by dismutation is also cleaved by alkali and gives an acid mixture much richer in *p*-phenylbenzoic acid than that obtained by cleavage of the pinacolones. A similar, apparently increased migration of the phenyl group could be obtained by using perchloric acid in acetic acid, if the rate of rearrangement was reduced by the addition of a little water. The widest difference in the values for migratory aptitudes with different reagents is encountered if *s*-di-*o*-phenylbenzopinacol is used for comparison. Agents other than perchloric acid bring about the pinacolone change so slowly that it is entirely displaced by side reactions. The presence of water in the perchloric acid solution also has a more pronounced effect here (Table II). Hydriodic acid in acetic acid, usually a satisfactory agent, failed in this case, and doubtless other pinacols exist where it causes partial dismutation and partial rearrangement. *s*-Di-*o*-fluorobenzopinacol appears to be of this class (Bergmann, *Rec. Trav. chim.*, 1939, **58**, 866). For these reasons data for

\* Marvel, Mueller, and Ginsberg (*loc. cit.*) considered that, if triarylmethyls owed their stabilities largely to resonance, then lack of conjugation in the *m*-diphenyl group would require that it confers no greater stability upon triarylmethyl radicals than does phenyl, a deduction which disagrees with their experimental finding: *m*-diphenyl > phenyl. Ingold and Burton (*loc. cit.*), in discussing the case of pentaphenylethyl, consider that stabilising influences due to resonance must be transmitted to some extent through two consecutive single bonds; by a similar argument it follows that the *m*-diphenyl group should confer greater stability than phenyl in the triarylmethyl series.

migratory aptitudes should generally be more trustworthy if perchloric acid has been used for the rearrangement.

TABLE I.  
*Rearrangements of s.-Di-p-phenylbenzopinacol.*

Rearranging agent.	Equivalent wt. of mixed acids.*	Yield of mixed acids, %.	Migratory aptitude of <i>p</i> -diphenyl.
2% Perchloric acid in anhyd. acetic acid .....	138 ± 0.5	84	3.75
Hydriodic acid in acetic acid .....	138 ± 0.5	83	3.75
<i>p</i> -Toluenesulphonic acid in acetic acid .....	137.5 ± 0.5	79	3.9
Acetyl chloride in benzene-acetic acid .....	148 ± 2	76	1.87
2% Perchloric acid in acetic acid + 4% of water ...	144 ± 2	73	2.6

\* The mean equivalent weight is given with the maximum experimental variation.

We have failed to confirm the migratory aptitude obtained by Gomberg and Bachmann (*loc. cit.*) for *p*-diphenyl. Their value demands an equivalent weight of 128 for the mixed acids obtained by scission, which differs considerably from ours (see Table I). Their low value is probably to be explained by the method of estimation used: the amount of *p*-phenylbenzoic acid in the mixture was determined by removing the benzoic acid present with warm water and weighing the residual acid. Unless considerable care is taken, large errors can occur in the determinations of migratory aptitudes and considerable disagreement concerning migratory aptitude values is to be found in the literature [see the values for *m*-tolyl, *m*-anisyl, and *p*-anisyl given by Bailar (*loc. cit.*), Bachmann and Moser (*loc. cit.*), and by Bachmann and Ferguson (*J. Amer. Chem. Soc.*, 1934, **56**, 2081)]. The value now obtained for the migratory aptitude of *p*-diphenyl destroys in several examples the agreement found by Bachmann and Moser between predicted and observed migratory aptitudes. To give one example: the percentage migrations of *p*-tolyl and *p*-diphenyl in the appropriate symmetrical tetra-arylpinacol were predicted as:  $\frac{94/6}{92/8} = \frac{58}{42}$ . The observed value was:  $\frac{57}{43}$ . The predicted figures with the new data are:  $\frac{94/6}{79/21} = \frac{81}{19}$ . To the many other cases where the agreement still holds we have, as yet, applied no test. However, where, as in the case of the migratory aptitudes, the values are known to be liable to errors of several units %, it seems somewhat forced to employ in these predictions migratory aptitudes derived (as in the above example) from acid mixtures of one-sided compositions. The effect of errors will be magnified. The agreements between predicted and observed values found by Bachmann mean either that the two aryl groups attached to the carbon atom on to which migration occurs are without influence upon the course of the rearrangement, or that their combined influences, chemical and steric, can be computed exactly from a comparison of each group separately with any arbitrarily selected third aryl group. The first alternative seems unlikely; in many cases the second may be approximately fulfilled, but that it should be fulfilled as closely as the experiments of Bachmann, Moser, and Ferguson indicate, seems, quite apart from the question of experimental error, hardly to be expected.

#### EXPERIMENTAL.

2-Phenylbenzophenone, m. p. 92°, was prepared according to the method of Schlenk, Bergmann, and Knorr (*Annalen*, 1928, **464**, 33), who give m. p. 90°. 2-Phenylbenzophenoneanil, obtained by boiling the ketone with excess of aniline and a little aniline hydrobromide for  $\frac{1}{2}$  hour in an atmosphere of carbon dioxide, was isolated by pouring the products into alcohol. It formed yellow crystals, m. p. 91–92° (Found: N, 4.1.  $C_{25}H_{19}N$  requires N, 4.2%).

2-Phenylbenzhydrol was obtained by reduction of 2-phenylbenzophenone with zinc dust and alcoholic potash at 30° for 5 days (Elbs, *J. pr. Chem.*, 1886, **33**, 184). It separated from light petroleum (b. p. 40–60°) in colourless crystals, m. p. 71° (Found: C, 87.3; H, 6.2; M, in camphor, 241.  $C_{19}H_{19}O$  requires C, 87.7; H, 6.2%; M, 260). When warmed for a few minutes with a 3 : 1 sulphuric-acetic acid mixture, the hydrol was completely converted into

9-phenylfluorene, m. p. and mixed m. p. 147°, which was isolated by pouring the mixture into water.

*s.-Di-o-phenylbenzopinacol* was prepared in three ways.

(1) 2-Phenylbenzophenone (30 g.) was shaken with zinc dust (45 g.) and acetic acid (350 c.c.) at 25–30° for 10 days. The mixture was poured into water, and the insoluble material collected, washed with a little alcohol, and extracted with boiling chloroform. Concentration of the extracts and addition of alcohol gave the desired pinacol (24 g.) as a mixture of two stereoisomers. The less soluble  $\alpha$ -form (1 part dissolves in 33 parts of boiling chloroform), present in much the larger quantity, was readily obtained pure, by repeated crystallisation from chloroform and alcohol, in small colourless needles, m. p. 175° (decomp.). The  $\beta$ -form was unstable, being converted into the  $\alpha$ -isomer in hot chloroform solution. It was extracted from the mixture of isomers with a warm 1 : 1 mixture of chloroform and alcohol and then caused to crystallise by the addition of an equal volume of alcohol. The  $\alpha$ -isomer still present was removed by submitting the crystals to repeated extractions of this kind, filtering each time from small amounts of the undissolved  $\alpha$ -isomer. Owing to its labile nature, even after repeated purification the  $\beta$ -form melted at 152–160°, but it was homogeneous and consisted of large, flat, hexagonal prisms.

(2) The ketone (2 g.), sodium (0.2 g.), and dry ether (15 c.c.) were shaken under nitrogen in a Schlenk tube for 4 days; the product, hydrolysed with aqueous acetic acid, yielded 0.45 g. of mixed stereoisomeric pinacols together with unchanged ketone (compare Bachmann, *J. Amer. Chem. Soc.*, 1933, 55, 1179).

(3) When the reaction between phenylmagnesium bromide (2 mols.) and methyl 2-phenylbenzoate (0.1 mol.) was carried out in an atmosphere of nitrogen and in presence of excess of magnesium, small yields (3%) of the mixed pinacols were obtained (compare Hatt, J., 1929, 1623). 2-Phenyltriphenylcarbinol, the chief product of the reaction, was identified by conversion with boiling acetic acid into 9 : 9-diphenylfluorene (m. p. 222°).

The pinacols were not produced by irradiation of 2-phenylbenzophenone in *isopropyl* alcohol. Gomberg and Clarkson (*J. Amer. Chem. Soc.*, 1930, 52, 2882) found that reduction of 2-phenylbenzophenone with magnesium and magnesium iodide gave only 9-phenylfluorene.

The  $\alpha$ -pinacol crystallised with one molecule of water, which was lost very slowly at 100°/1 mm. over phosphoric oxide (higher temperatures were not used for fear of thermal dismutation). Attempts to detect this water by the Zerewitinov determination with diisomyl ether as solvent were only partially successful, probably because of the insolubility of the pinacol [Found : active H, 2.3, 2.5.  $C_{38}H_{30}(OH)_2 \cdot H_2O$  requires active H, 4.0. Under the same conditions benzopinacol gave : active H, 1.97, 1.90. Calc. for  $C_{26}H_{20}(OH)_2$  : active H, 2.0. Found for the  $\alpha$ -pinacol hydrate : C, 84.9, 84.9 (84.8 by A. Schoeller); H, 5.9, 5.7 (5.7 by A. Schoeller).  $C_{38}H_{30}O_2 \cdot H_2O$  requires C, 85.1; H, 6.0%].

The  $\beta$ -pinacol also crystallised with a molecule of water (Found : loss at 100° in a vacuum over phosphoric oxide, 3.8.  $C_{38}H_{30}O_2 \cdot H_2O$  requires  $H_2O$ , 3.4. Found for the anhydrous material : C, 87.7; H, 5.8.  $C_{38}H_{30}O_2$  requires C, 88.0; H, 5.8%).

Conversion of the  $\beta$ - into the  $\alpha$ -pinacol was complete after a dilute solution of the  $\beta$ -pinacol, m. p. 152–158°, in chloroform had been refluxed for 8 hours on a water-bath. Evaporation and addition of alcohol caused crystallisation of the  $\alpha$ -pinacol, m. p. 175°. Unchanged  $\beta$ -form could not be detected.

*Oxidation of the pinacols.* The  $\alpha$ - or the  $\beta$ -pinacol (0.3 g.), iodine (0.25 g.), and a 20% solution of sodium acetate in acetic acid (5 c.c.) were refluxed for 1 hour, and the mixture poured into dilute sulphurous acid. The 2-phenylbenzophenone obtained (0.28 g.) melted at 92° after one recrystallisation from light petroleum.

*3-Phenylbenzophenone* was prepared from 3-diphenylmagnesium bromide and benzonitrile. No difficulty was encountered in the preparation of the Grignard reagent if the reaction was carried out in an atmosphere of nitrogen, the magnesium activated by the method of Baeyer, and completely dry reaction vessels used with reagents that had been dried by heating at 100° in small closed flasks, in the air spaces of which were suspended small tubes containing phosphoric oxide.

3-Bromodiphenyl (46.7 g.), activated magnesium (4.8 g.), and ether (140 c.c.) were allowed to react and the mixture was refluxed for 2 hours after the vigorous reaction had subsided. Benzonitrile (13.5 g.) in ethereal solution was added slowly with stirring. After refluxing (8 hours), the product was decomposed with ice and dilute acid, the ether removed, and the residual ketimine hydrolysed with hot aqueous acid (6 hours). The ketone was obtained by fractional distillation of the products. It formed a pale yellow oil, b. p. 264–267°/25 mm., and separated from light petroleum (b. p. 80–100°) in colourless crystals, m. p. 79°. Yield,



23.5 g. (46%) (Found: C, 88.6; H, 5.5; *M*, in camphor, 267.  $C_{18}H_{14}O$  requires C, 88.4; H, 5.5%; *M*, 258).

**3-Phenylbenzhydrol**, prepared from 3-phenylbenzophenone according to the method given for 2-phenylbenzhydrol, crystallised from light petroleum (b. p. 60–80°) in fine white needles, m. p. 81°. In sulphuric acid it gave a deep red solution (Found: C, 88.1; H, 6.4.  $C_{19}H_{16}O$  requires C, 87.7; H, 6.2%).

**s.-Di-m-phenylbenzopinacol**.—The method of Gomberg and Bachmann (*J. Amer. Chem. Soc.*, 1927, **49**, 236) proved unsuitable for this pinacol. Small yields of the compound with larger quantities of the hydrol were obtained by reduction of the ketone with zinc dust and acetic acid at 15–20° for several days. The pinacol was separated from admixed hydrol by crystallisation from chloroform and alcohol (yield, 20%).

Larger yields (55%) were obtained by photochemical reduction of 3-phenylbenzophenone in isopropyl alcohol (compare "Organic Syntheses," **14**, 8). The pinacol separated from chloroform and alcohol in rosettes of fine needles, m. p. 178°. These gave no colour with sulphuric acid, but dissolved in warm alcoholic potash with a transient blue coloration (Found: C, 88.2; H, 5.9.  $C_{28}H_{20}O_2$  requires C, 88.0; H, 5.8%). The pinacol was completely oxidised by iodine and sodium acetate in acetic acid solution to 3-phenylbenzophenone.

**s.-Di-p-phenylbenzopinacol**.—This was prepared by the method of Gomberg and Bachmann (*loc. cit.*). It may also be readily obtained (45% yield) by reduction of 4-phenylbenzophenone with zinc dust in acetic acid at 37°. The pinacol used in the rearrangements was crystallised from chloroform and alcohol or from dioxan and ether and melted at 198–201°.

**Rearrangement of the Pinacols**.—In the general procedure using perchloric acid, the pure pinacol (1.5 g.), dried at 80° in a vacuum, was added to an anhydrous 2% solution of perchloric acid in acetic acid, obtained by mixing acetic acid (14 c.c.), acetic anhydride (13 c.c.), and 20% aqueous perchloric acid (3 c.c.). The mixture was refluxed in an all-glass apparatus on an oil-bath for 1 hour and then poured into water. The precipitated pinacolones, after standing, were collected on a sintered-glass crucible, washed thoroughly, and dried to constant weight at 100°. The yields of pinacolones were usually about 98%.

When hydriodic acid was used, 0.1 c.c. of constant-boiling (*d* 1.7) acid was added to 20 c.c. of acetic acid and used to rearrange 1.0–1.3 g. of pinacol. The reaction mixture was heated as stated in the previous case, but for a longer time (6 hours). The reaction mixture was poured into water containing a little sodium bisulphite, and the product collected as already described. When s.-di-o-phenylbenzopinacol was refluxed with this reagent for 20 hours, the only product that could be identified was 2-phenylbenzophenone.

In rearrangements with *p*-toluenesulphonic acid, the dry acid (1.4 g.) was dissolved in acetic acid (40 c.c.) and used to rearrange the pinacol by heating under the conditions given above for 6 hours. s.-Di-o-phenylbenzopinacol under these conditions gave an oil containing 9-phenylfluorene.

Acetyl chloride in benzene-acetic acid solution was used following as far as possible the directions of Gomberg and Bachmann (*loc. cit.*). In order to free the pinacolones from contaminating acetic acid and acetic anhydride, it was necessary to boil for prolonged periods with water prior to collection of the pinacolones.

**o-Phenylbenzoyldiphenyl-o-diphenylmethane** was the sole product of the rearrangement of s.-di-o-phenylbenzopinacol with perchloric acid. It separated from acetic acid in colourless hexagonal plates, m. p. 195.5° (Found: C, 90.8; H, 5.8.  $C_{28}H_{20}O$  requires C, 91.2; H, 5.6%).

The mixture of pinacolones obtained from s.-di-m-phenylbenzopinacol was a glass which slowly crystallised from chloroform and methyl alcohol.

**Fission of the Pinacolones**.—o-Phenylbenzoyldiphenyl-o-diphenylmethane was unchanged after refluxing for 300 hours with 10% alcoholic or methyl-alcoholic potash. Fission was possible either with potassium hydroxide, with a little isoamyl alcohol added, at 185–195° (Fischl, *Monatsh.*, 1914, **35**, 524; Madelung and Oberwegner, *Ber.*, 1927, **60**, 2490), or with a mixture of potassium and sodium hydroxides (1:1) at the same temperature. The first reagent proved unsuitable for quantitative work, since appreciable amounts of isovaleric acid were formed during its use. s.-Di-m-phenyl- and s.-di-p-phenylbenzopinacol were rearranged with perchloric acid, and the equivalent weights of the acids obtained by fission of the pinacolones with potassium and sodium hydroxides (1:1) and with methyl-alcoholic potash compared. These were 176.5 and 173.3 with the first, and 143 and 144.7 with the second pinacolone. They agree within the limits of experimental error. That the mixed acids produced in the fission suffered no decomposition was shown by fusing synthetic mixtures of *p*-phenylbenzoic acid and benzoic acid with alkali and recovering the acids (Found: equiv., 140.1. Calc., 140.6).

In the method used, the pinacolone (1.2—1.5 g.) and powdered potassium and sodium hydroxides (1 : 1) (8 g.) were heated in a Palau test-tube contained in an oil-bath at 185—195°. After 2.5 hours, during which time the mixture was frequently stirred, the products were extracted with water, the methanes filtered off, and if necessary completely removed by a subsequent extraction with benzene. The acids were liberated with concentrated hydrochloric acid and extracted in benzene, the combined benzene liquors washed twice with water, dried over sodium sulphate, and evaporated on a water-bath, and the residue dried to constant weight in a vacuum desiccator (4 days) and titrated with standard barium hydroxide. The benzene distillate always contained small amounts of benzoic acid, which was estimated by titration and a correction applied.

TABLE II.

Rearranging agent.	No. of determinations.	Equiv. wt. of mixed acids.*	Yield of acids, %.	Migratory aptitude (Ph = 1).
<i>Rearrangement of s-Di-o-phenylbenzopinacol.</i>				
2% Perchloric acid in anhyd. acetic acid .....	4	192 ± 4	87—90	<i>o</i> -Diphenyl = 0
2% Perchloric acid in acetic acid + 4% of water	3	178 ± 3	84—93	—
<i>Rearrangement of s-Di-m-phenylbenzopinacol.</i>				
2% Perchloric acid in anhyd. acetic acid .....	4	176 ± 3	72—84	<i>m</i> -Diphenyl = 0.41
2% Perchloric acid in acetic acid + 4% of water	1	175.4	75	<i>m</i> -Diphenyl = 0.42
Hydriodic acid in acetic acid .....	2	170 ± 1	78 and 89	<i>m</i> -Diphenyl = 0.58

\* The mean equivalent weight is given with the maximum experimental variation.

These results show that the equivalent weight of the mixed acids from the *o*-substituted pinacol is altered considerably by the presence of water in the acetic acid. This pinacol would also be expected to dismute rapidly at the temperature used for rearrangement (compare Bergmann, *Rec. Trav. chim.*, 1939, 58, 866). Accordingly *o*-diphenyl is assigned a migratory aptitude of zero.

*2-Phenyltriphenylmethane*, obtained from fission of *o*-phenylbenzoyldiphenyl-*o*-diphenylmethane, crystallised from chloroform and methyl alcohol in colourless hexagonal plates, m. p. 138° (Found: C, 93.4; H, 6.6.  $C_{25}H_{20}$  requires C, 93.7; H, 6.3%).

*Alkaline Fission of Phenyl-substituted Benzophenones*.—Dismutation to ketone and hydrol appears to be the chief side reaction in the rearrangement of a pinacol. Since ketones are cleaved by alkali fusion, in order to determine the effect ketonic impurities would have on the equivalent weights of acids from the pinacolone fission, the pure ketones were submitted to alkaline fission. 1 G. of the ketone and 8 g. of the fusion mixture were heated in exactly the manner used in pinacolone fission and the equivalent weight of the mixed acids was determined as described there:

Ketone.	% Yield of acids.	Equiv. wt. of mixed acids.
2-Phenylbenzophenone .....	70—72	128.9, 126.5, 128
3-Phenylbenzophenone .....	65—80	166.8, 164.3, 165.3
4-Phenylbenzophenone .....	55—59	175.2, 178

The equivalent weights of the acid mixtures from 2- and 4-phenylbenzophenones differ so widely from those of the acids obtained from the corresponding pinacolone fission that small amounts of these ketones in the pinacolones will introduce considerable error in the values for the migratory aptitudes. Our equivalent weight for the cleavage acids from 4-phenylbenzophenone (177) differs considerably from that of Bachmann (160.8) (*J. Amer. Chem. Soc.*, 1935, 57, 737).

We wish to thank the Chemical Society for a research grant.

THE UNIVERSITY OF MELBOURNE.

[Received, April 24th, 1941.]