of a relatively low hydrogen-ion concentration and permits the oxidation of compound reducing aldoses, such as lactose, without complications from hydrolysis. The reaction mixture should be kept in the dark for best results. The yields of aldonic acid are nearly quantitative. In the case of lactose it is possible to oxidize it to nearly pure lactobionic acid, which can then be hydrolyzed to galactose and gluconic acid, both of which can be obtained in high yield. It is believed that the new directions make the method of bromine oxidation of aldoses much more precise and suitable for a wide range of preparations. Examples of the oxidation of glucose, xylose and lactose are given. It is suggested that the improved directions may be found suitable for laboratory instruction in sugar chemistry as well as for research.

WASHINGTON, D. C.

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

HALOGEN-SUBSTITUTED AROMATIC PINACOLS AND THE FORMATION OF KETYL RADICALS, $R_2(IMgO)C—$

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It has been shown that aromatic ketones may be reduced to pinacols by a binary system consisting of a mixture of magnesium iodide and magnesium in anhydrous solvents[2]

$$2R_2CO \xrightarrow[Mg]{MgI_2} R_2(IMgO)C—C(OMgI)R_2 \xrightarrow{H_2O} R_2(HO)C—C(OH)R_2 + 2Mg(OH)I \quad (1)$$

We now find that this method can be applied to the preparation even of some of the halogenated pinacols with considerable success.

The decisive color effects given by some of our pinacols afforded an opportunity to test, by the application of Beer's law, the hypothesis that halomagnesium pinacolates dissociate into ketyls

$$R_2(IMgO)C—C(OMgI)R_2 \rightleftharpoons 2R_2(IMgO)C— \quad (2)$$

In the field of the pinacolin rearrangement, various investigators have reported upon the relative migratory tendency of bromophenyl and phenyl groups[3], and upon that of phenyl and biphenyl groups.[4] We have now studied the relative migratory tendencies of bromophenyl and biphenyl groups, in order to compare the actual findings with the predictions.

Preparation of the Halogen-Substituted Pinacols.—For preparative purposes, best results are obtained with tolerably concentrated solutions

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[1] The material here presented is from a dissertation submitted by John C. Bailar, Jr., to the Faculty of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1928.

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

[3] Montagne, *Rec. trav. chim.*, **29**, 150 (1910); Koopal, *ibid.*, **34**, 115 (1915).

[4] Ref. 2, p. 251.

of the ketones and magnesium iodide, and with the metal in the form of powder; the reduction is complete in a few hours, especially when the mixture is heated. However, for the study of the mechanism of the reaction, a modified procedure has been used in order to obtain further evidence whether the amount of magnesium consumed by the reduction fulfils the conditions of the hypothesis (Equation 1), and also in order to determine to what extent the halogen in the ketone molecule is detached from the benzene nucleus. Obviously, if no such halogen be split off, then for each equivalent of metallic magnesium consumed one equivalent of hydroxide ion should be formed on hydrolysis of the glycolate, and one mole of the ketone should be reduced to pinacol. On the other hand, if, in addition to reduction of the CO group, some halogen in the ring is removed, the amount of magnesium dissolved will be larger, and will be equivalent to the sum of the hydroxide ion and halide ion detached from the nucleus.

These measurements were carried out in the following manner. Somewhat more than 0.01 of a gram atom of iodine and an excess of magnesium powder were allowed to react in anhydrous ether, and the colorless solution was filtered into a 100-cc. graduate. Ordinarily most of the ether was boiled off and the solution was diluted to a known volume with dry benzene, retaining just enough ether to keep the magnesium iodide in solution. Two cc. of the solution was pipetted out and titrated for halide and the amount of the halide in the remaining solution was calculated. To this solution was added 0.01 of a gram molecule of the ketone and a weighed amount of magnesium shavings; the graduate was stoppered and shaken until the reaction was certain to have become complete. When the magnesium shavings remaining had settled, most of the liquid was pipetted off and quickly poured into water containing a known amount of standard sulfuric acid. The water layer was diluted to 500 cc. Of this, 100 cc. was titrated with sodium hydroxide and 25 cc. with silver nitrate. Simple calculation indicates how many equivalents of hydroxide ion have been produced by the hydrolysis of the pinacolate, and possibly other organomagnesium compounds, and how many equivalents of halide have been liberated from the ring. The magnesium shavings were filtered from the remaining liquid, quickly washed with ether, alcohol and water, then dried and weighed. The benzene layer was dried and allowed to evaporate. The product was macerated with petroleum ether or with alcohol in order to remove any unchanged ketone, and the pinacol remaining weighed.

It has been found that while *m*- and *p*-halogenated ketones are reduced to the corresponding pinacols, in the *o*-substituted ketones the halogen in the nucleus is also attacked by the magnesium. The reduction of the halogen-substituted ketones proceeds much more slowly than in the case of the ketones that Gomberg and Bachmann reduced. Instead of a few minutes, some of the bromobenzophenones are not completely reduced, even after shaking for several hours.

Gomberg and Bachmann reported that magnesium bromide can be substituted for the iodide in this reaction; the only difference is in the speed of the reduction. In the case of the halogenated benzophenones this does not seem to be the case. The conditions were varied widely in regard to concentration, time and temperature, but in every instance the ketone was recovered unchanged. This failure of magnesium bromide to react may be due to the extreme insolubility of the double compounds formed between the ketones and magnesium bromide.

***Sym*.-4,4′-dibromobenzopinacol.**—This was prepared from 4-bromobenzophenone in accordance with the general directions. One one-hundredth of a mole of ketone gave rise to 0.009 equivalents (0.0045 mole) of the pinacol and 0.0093 equivalents of $(OH)^-$, and there was consumed 0.0095 equivalent of magnesium. No ring halogen was taken out by the metallic magnesium. In nearly all of the experiments, as in this one, slightly more than the theoretical quantity of magnesium was consumed. This discrepancy is explained if the formation of magnesium oxide, by the air left in the reaction vessel, is considered. When working with larger amounts and magnesium powder, the yield of pure product was 94%; and the crystals of the pinacol melted at 178°, as given by Montagne.

***Sym*.-3,3′-dibromobenzopinacol.**—*m*-Bromobenzophenone gave with magnesium iodide a white double compound that did not completely dissolve until after three days. It was found that from 0.01 mole of ketone, 0.01 equivalent of pinacol had been produced, 0.0104 equivalents of magnesium had been used up, and no bromine had been removed from the benzene ring in the ketone molecule.

In another experiment 5.2 g. of the ketone was reduced in 60 cc. of solution in a few hours. The pinacol melted sharply at 147°, as Koopal has previously found. The yield of pure product was 85%.

Reduction of 2-Bromo- and of 2-Chlorobenzophenones by the Binary System.—The bromine atom of 2-bromobenzophenone is so labile that it may be removed almost completely from the molecule by the action of the magnesium and magnesium iodide mixture, although magnesium alone has no effect, even upon boiling for several days. It was never possible to get more than a very small amount of pinacol; this melted at 160–165°, as compared with 168° as given by Koopal.

A mixture of magnesium and magnesium bromide gave equally unsatisfactory results. In one experiment the vessel was heated to 70° for a week. The solution became pink but when the mixture was hydrolyzed it was found that no reduction had taken place, but that 17.5% of the ketone had been destroyed through loss of nucleus bromine.

2-Chlorobenzophenone behaves like its bromo-analog and repeated experiments indicated that a large amount of chlorine had been removed from the benzene nucleus.

This result with the *o*-halogeno-benzophenones is in harmony with other instances of lability of halogen atoms ortho to the carbonyl group. In addition to the well-known Ullmann syntheses from *o*-chlorobenzoic acid, one may mention the experience of Montagne and van Charante,[5] of Simonis and Kirschten[6] and of Zal'kind and Schmidt.[7]

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[5] Montagne and van Charante, *Rec. trav. chim.*, **31**, 300 (1912).

[6] Simonis and Kirschten, *Ber.*, **45**, 567 (1912).

[7] Zal'kind and Schmidt, *J. Russ. Phys.-Chem. Soc.*, **46**, 681 (1914).

4,4',4'',4'''-Tetrabromobenzopinacol.—Magnesium iodide and 4,4'-dibromobenzophenone form a yellow double compound. After six hours' shaking with metallic magnesium the precipitate was completely dissolved and the solution was clear bright red; after ten hours more it was hydrolyzed. The pinacol melted at 179–180°, as Montagne[8] has reported. The yield of pure product was 94%.

The quantitative relationships involved are normal. From the reaction with 0.01 mole of ketone there was obtained 0.0091 equivalent of pinacol and 0.0091 equivalent of magnesium were used up. No bromide ion was present in the aqueous solution.

3,3'-Dibromobenzophenone.—To the Grignard reagent from 20 g. of *m*-dibromobenzene and 2 g. of magnesium was added an ether solution of 15.4 g. of *m*-bromocyanobenzene. The solution was refluxed for several hours and then hydrolyzed. After three recrystallizations from alcohol, the ketone melted sharply at 140°.[9] The yield of pure material was 13.7 g. or 46%. From the mother liquors was obtained a small amount of a substance consisting of very fine needles, m. p. 172°, doubtless the diketone, *m*-$BrC_6H_4COC_5H_4COC_6H_4Br$-*m*, (CO:CO = 1:3).

Anal. Calcd. for $C_{13}H_8OBr_2$: Br, 47.06. Found: Br, 47.20. *Mol. wt.* in benzene. Calcd.: 340. Found: 341. *Anal.* of diketone. Calcd. for $C_{20}H_{12}O_2Br_2$: Br, 36.04. Found: Br, 35.70.

3,3',3'',3'''-Tetrabromobenzopinacol.—In the process of reduction the solution assumed a bright red color and after five days the double compound, ketone + MgI_2, had completely dissolved. The pinacolate was hydrolyzed in the usual way; it was found that no halogen had been removed from the ketone molecule and that the calculated amount of magnesium was used up. The pinacol was exceedingly difficult to purify and only 40% of the crystalline product could be obtained pure. After recrystallization from a mixture of alcohol and chloroform, it melted at 152–156°.

Anal. Calcd. for $C_{26}H_{18}O_2Br_4$: Br, 46.92. Found: Br, 46.99. *Mol. wt.* in benzene. Calcd.: 682. Found: 658.

3,4'-Dibromobenzophenone.—A mixture of 20 g. of 3-bromobenzoyl chloride, 50 cc. of bromobenzene and 14 g. of aluminum chloride was heated on the steam-bath for three days. The ketone was recrystallized from alcohol and then from benzene; the yield was 49%; m. p. 132°.[10]

For the purpose of verifying the constitution, the same ketone was prepared by the Grignard reaction, from *p*-dibromobenzene and *m*-bromocyanobenzene. After successive recrystallizations from benzene, acetone and alcohol, pure ketone was obtained, m. p. 130–131°. Mixed with the product obtained by the method of Friedel and Crafts, it melted at the same temperature. Here again a small amount of the diketone, *m*-$BrC_5H_4COC_6H_4COC_6H_4Br$-*m*, was formed (CO:CO = 1:4); m. p. 217–220°.

Anal. Calcd. for $C_{13}H_8OBr_2$: Br, 47.06. Found: Br, 47.09. *Mol. wt.* in benzene. Calcd.: 340. Found: 343. *Anal.* of diketone. Calcd. for $C_{20}H_{12}O_2Br_2$: Br, 36.04. Found: Br, 36.47.

Sym.-**3,3',4,''4'''-Tetrabromobenzopinacol.**—The reduction of 3,4'-dibromobenzophenone proved to be a very difficult problem, although the 4,4'-dibromo- and the 3,3'-dibromobenzophenones offered no difficulty. A solution of a large excess of magnesium iodide, from 8 g. of iodine and an excess of magnesium powder, in 50 cc. of ether was diluted to 100 cc. with benzene and 1 g. of the ketone was added. The vessel was tightly stoppered and the solution was heated to 75° for four days. At the end

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[8] Montagne, *Rec. trav. chim.*, **43**, 640 (1924).

[9] Demuth and Dittrich, *Ber.*, **23**, 3614 (1890).

[10] Kunckell, *ibid.*, **37**, 3485 (1904).

of the first day a pink color had developed—this gradually darkened to deep red. Although the reduction had proceeded to the extent of 76%, only about 35% of the material could be obtained crystalline; m. p. 160–163°. No bromine was detached from the ketone.

Anal. Calcd. for $C_{26}H_{18}O_2Br_4$: Br, 46.92. Found: Br, 47.17. *Mol. wt.* in benzene. Calcd.: 682. Found: 686.

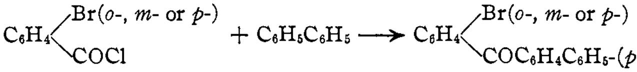
4-Chloro-4′-bromobenzophenone.—This ketone was prepared from 4-bromobenzoyl chloride, chlorobenzene and aluminum chloride. After recrystallization from alcohol and then from benzene it melted at 150°. The yield of pure product was 60%. The identical ketone was also prepared from 4-chlorobenzoyl chloride and bromobenzene.

Anal. Calcd. for $C_{13}H_8OBrCl$: Br, 27.07; Cl, 12.01. Found: Br, 27.46; Cl, 11.85. *Mol. wt.* in benzene. Calcd.: 295.5. Found: 289.

Sym.-**4,4′-dichloro-4″,4‴-dibromobenzopinacol.**—With magnesium shavings the reduction is somewhat slow, but after eight hours' shaking with magnesium powder the yield of the pinacol is quantitative. The halogen in the benzene nucleus is not affected by the metallic magnesium. The pinacol is crystallized from ether or acetone and melts at 169°.

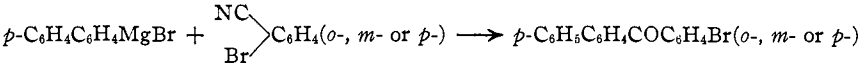
Anal. Calcd. for $C_{26}H_{18}O_2Br_2Cl_2$: Br, 26.98; Cl, 11.97. Found: Br, 26.52; Cl, 12.26. *Mol. wt.* in benzene. Calcd.: 593. Found: 633.

4-Bromo-4′-phenylbenzophenone, 3-Bromo-4′-phenylbenzophenone and 2-Bromo-4′-phenylbenzophenone.—These three ketones were prepared according to the reaction



$$C_6H_4\left\langle\begin{matrix}\text{Br}(o\text{-}, m\text{- or } p\text{-})\\ \text{COCl}\end{matrix}\right. + C_6H_5C_6H_5 \longrightarrow C_6H_4\left\langle\begin{matrix}\text{Br}(o\text{-}, m\text{- or } p\text{-})\\ \text{COC}_6\text{H}_4\text{C}_6\text{H}_5\text{-}(p)\end{matrix}\right.$$

The acid chloride from 20 g. of the corresponding bromobenzoic acid was dissolved in 150 cc. of carbon disulfide, 20 g. of biphenyl was added, and then 16 g. of aluminum chloride, in small portions. The mixture was warmed on the steam-bath for three days. After hydrolysis, the unchanged biphenyl was removed by distillation under reduced pressure. The ketones may then also be distilled under reduced pressure, though their boiling points are very high (near 300° at 15–18 mm.), or they may be purified by crystallization from alcohol or benzene. The yields were *o*-bromo-, 65; *m*-, 75 and *p*-, 55%. In order to verify the structure of the ketones they were prepared also from *p*-biphenylmagnesium bromide and the corresponding bromocyanide



$$p\text{-}C_6H_4C_6H_4MgBr + \begin{matrix}\text{NC}\\ \text{Br}\end{matrix}\!\!\left.\right\rangle C_6H_4(o\text{-}, m\text{- or } p\text{-}) \longrightarrow p\text{-}C_6H_5C_6H_4COC_6H_4Br(o\text{-}, m\text{- or } p\text{-})$$

The materials prepared by the two different methods melted at the same temperature in every case and mixed melting points showed no depression. The melting points, analyses and molecular weights are:

Ketone, $C_9H_{13}OBr$	M. p., °C.	Bromine Calcd.	Bromine Found	Mol. wt. Calcd.	Mol. wt. Found
Ortho	88.5	23.74	23.84	337	343
Meta	119		23.74		339
Para	188		23.55		334

Sym.-**4,4′-Dibromo-4″,4‴-Diphenylbenzopinacol.**—4-Bromo-4′-phenylbenzophenone, subjected to the action of the binary system, gave a light green solution of the ketyl. No bromine had been removed from the ketone molecule. The loss in weight of the magnesium and the amount of pinacol corresponded each to 0.009 equivalent. The pinacol melts at 158–159°.

Anal. Calcd. for $C_{38}H_{28}O_2Br_2$: Br, 23.67. Found: Br, 23.56. *Mol. wt.* in benzene. Calcd.: 676. Found: 652.

Sym.-**3,3′-Dibromo-4″,4‴-Diphenylbenzopinacol.**—This was obtained by reduction of the 3-bromo-4′-phenylbenzophenone in a solution containing largely benzene and but little ether. The yield of pinacol was 64%; m. p. 175°.

Anal. Calcd. for $C_{38}H_{28}O_2Br_2$: Br, 23.67. Found: Br, 23.63. *Mol. wt.* in benzene. Calcd.: 676. Found: 662.

Reduction of 2-Bromo-4′-Phenylbenzophenone.—This ketone, which contains a bromine atom ortho to the carbonyl group, offered the same difficulties as the 2-bromo- and 2-chlorobenzophenones. Bromine was removed from the ketone and no pinacol could be isolated.

Colorimetric Study of the Iodomagnesium Pinacolates

The iodomagnesium pinacolates are colorless in the solid state but when dissolved impart color to the solution. In this respect they behave very much like so many of the hexa-arylethanes, and, like the latter, they are assumed to dissociate with the production of free radicals; in this case the ketyls of the type $R_2C(OMgI)$, Equation 2. Unfortunately, it has not proved possible to isolate the pinacolates in such a degree of purity that molecular weight determinations could serve as definite proof of their dissociation. We have therefore sought to determine whether the color of solutions of pinacolates is intensified on dilution. Such deviation from Beer's law has, in many cases, furnished the only means of detecting changes on dilution, that is, dissociation into free radicals. Four iodomagnesium pinacolates, namely, those prepared from benzophenone, 4-bromobenzophenone, 4-chloro-4′-bromobenzophenone and 4-bromo-4′-phenylbenzophenone, have been studied from the point of view of Beer's law. The solutions of all of these pinacolates are red.

We have used the colorimeter previously described,[11] but so modified for the present purposes that, instead of solid pinacolates, the reduction solutions of the ketones could be introduced directly into the colorimeter. The ketone was reduced by means of the binary system in a Drechsel bottle; one arm of this was then connected with appropriate stopcocks to a hydrogen pressure tank and the other led to a filtering tube, from which the pinacolate solution could be discharged into each of the two comparator tubes and into the reservoir.

The iodomagnesium pinacolates are extremely sensitive to traces of air and great care was necessary in order to avoid decolorization of the solution. The entire system was repeatedly evacuated and filled with hydrogen. During the course of the experiment the apparatus was always kept under a positive pressure of hydrogen. All rubber connections were made of the best material available and were coated at the joints

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[11] Gomberg and Sullivan, THIS JOURNAL, **44**, 1825 (1922).

with paraffin or de Khotinsky cement. In some of the earlier experiments the filtering funnel was fitted with hardened filter paper instead of the alundum disk, as in the latter experiments, but it was found that the traces of air adsorbed by the paper were sufficient to decolorize a dilute solution of the pinacolate. The hydrogen was purified by passing over a red-hot copper spiral and through concentrated sulfuric acid. The solvent used for diluting the solutions was freed from dissolved air by bubbling pure hydrogen through it. Part of the pinacolate solution was forced through the filter tube into that arm (B) of the colorimeter where dilutions were to be made, the remainder into the reservoir. The liquid in the reservoir could then be raised into the second arm (A) of the colorimeter by pressure of hydrogen until the depth of color appeared the same in the two colorimeter tubes. Solvent was then forced into the colorimeter tube B and, when equilibrium had been established, the

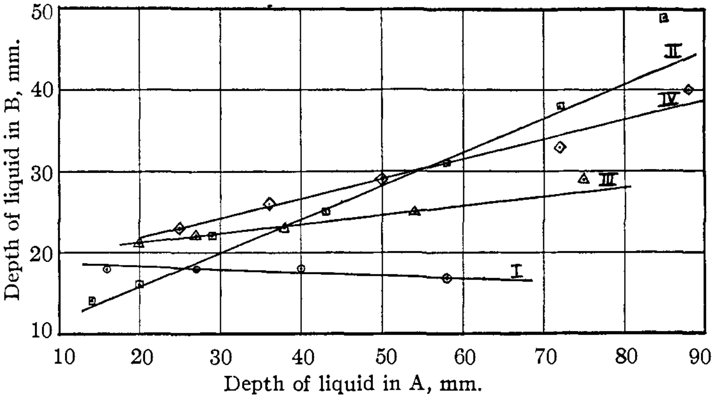
TABLE I

CHANGE OF COLOR WITH DILUTION

Benzopinacolate **Depth in mm.**		*Sym.*-4,4′-dibromobenzopinacolate Depth in mm.		*Sym.*-4,4′-dichloro-4″,4‴-dibromobenzopinacolate Depth in mm.		*Sym.*-4,4′-dibromo-4″,4‴-diphenylbenzopinacolate Depth in mm.	
B	**A**	B	A	B	A	B	A
Ketone—7.5 g.		Ketone—1 g.		Ketone—4 g.		Ketone—4 g.	
Iodine—7.5 g.		Iodine—1.5 g.		Iodine—4 g.		Iodine—4 g.	
15	14	14	8	20	21	23	22
24	13	29	12	27	22	33	26
37	13	45	17	38	23	52	35
55	11	58	19	54	25	65	40
		73	27	75	29		
Ketone—3 g.		Ketone—1 g.		Ketone—4 g.		Ketone—4 g.	
Iodine—3 g.		Iodine—1.5 g.		Iodine—4 g.		Iodine—4 g.	
16	18	10	10	18	19	25	23
27	18	25	16	34	22	36	26
40	18	38	17	48	25	50	29
58	17	50	20	74	31	72	33
		64	22			88	40
Ketone—2 g.		Ketone—1 g.				Ketone—7.5 g.	
Iodine—2 g.		Iodine—1.5 g.				Iodine—7.5 g.	
28	30	14	14			19	16
34	32	20	16			28	19
40	33	29	22			37	23
48	33	43	25			49	26
		58	31			68	28
Ketone—10 g.		72	38				
Iodine—10 g.		85	49				
22	22	Ketone—4 g.					
29	22	Iodine—4 g.					
38	20	22	22				
50	22	30	25				
		44	31				

depth of color in the two tubes was again compared and another dilution was made. The average of four or more readings is recorded in the table, the individual readings agreeing within one mm.

The results of typical experiments on each of the ketones studied are shown graphically in Fig. 1. They show unmistakably that in three of the four cases increase of color occurs. Consequently, the pinacolates dissociate on dilution, producing iodomagnesium ketyls.

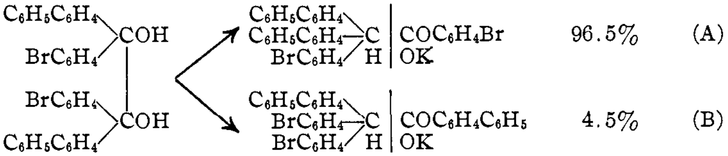


I, ⊙, Benzopinacolate; II, ⊡, 4-4′-dibromo-*sym.*-benzopinacolate; III, △, 4-4′-dichloro-4″,4‴-dibromo-*sym.*-benzopinacolate; IV, ◇, 4-4′-dibromo-4″, 4‴-diphenyl-*sym.*-benzopinacolate.

Fig. 1.

Comparative Migratory Tendencies of the Phenyl, *p*-Biphenyl, *p*-Bromophenyl and *m*-Bromophenyl Groups.—Montagne[3] has compared the migratory tendencies of the *p*-bromophenyl and the phenyl groups by rearranging the appropriate pinacol, and has found that 42 to 43% of the rearrangement is due to the migration of the *p*-bromophenyl group and 57 to 58% to that of the unsubstituted phenyl group. This work has been repeated and Montagne's results have been checked; our results have shown 41% of the migration due to the bromophenyl group and 59% to the phenyl group. Koopal has compared the migratory tendencies of the phenyl and the *m*-bromophenyl groups and has reported that only the substituted group migrates. This result has also been substantiated. Gomberg and Bachmann have shown that in the rearrangement of 4,4′-*sym.*-diphenylbenzopinacol, 92% of the migration is due to the *p*-phenyl-phenyl group and 8% to the unsubstituted group. Taking the migratory tendency of the phenyl group as 1, we may arrange the other groups as follows: *p*-bromophenyl, 0.695; *m*-bromophenyl, 0; *p*-phenyl-phenyl, 11.5. From these one may predict that the migratory tendencies of the *p*-bromophenyl and *p*-phenyl-phenyl groups should be in the relation of 1:16.5. Also, in a pinacol with a *m*-bromophenyl and *p*-phenyl-phenyl group, the latter group exclusively will migrate in the pinacolin rearrangement. Our actual results gave for the first case, 21.5 instead of 16.5; for the second, complete corroboration.

Rearrangement of *Sym.*-4,4′-Dibromo-4″,4‴-Diphenylbenzopinacol.—Two grams of the pinacol was dissolved in a mixture of 40 cc. of benzene, 10 cc. of acetic acid and 20 cc. of acetyl chloride, and the solution was boiled gently for eight hours. The liquid was evaporated and the crystalline residue of the pinacolins was boiled twelve hours with alcoholic potassium hydroxide. After removal of the triarylmethane compound, the resulting acids were separated from each other by converting the phenylbenzoic acid into the insoluble barium salt. We obtained 0.038 g. of this salt (which is equivalent to 0.028 g. of the phenylbenzoic acid) and 0.589 g. of bromobenzoic acid. This corresponds to 4.5 and 96.5%, respectively. The migratory tendencies are as 1:21.5. The pinacolin (A), recrystallized from glacial acetic acid, melts at 227°.



Anal. Calcd. for $C_{38}H_{26}OBr_2$: Br, 24.32. Found: Br, 23.97. *Mol. wt.* in benzene. Calcd.: 658. Found: 637.

The methane compound that was obtained by the splitting of the pinacolin was recrystallized from glacial acetic acid and melts at 186°. Since this substance has not been described, it was synthesized from biphenyl-*p*-magnesium bromide and the methyl ester of *p*-bromobenzoic acid. The 4,4′-diphenyl-4″-bromotriphenylcarbinol that resulted melted at 248–250°; reduced by means of zinc and glacial acetic acid, it gave the methane, which after purification melted at 186°. Rearrangement of the pinacol by acetic acid and iodine gave the same pinacolin.

Anal. of Carbinol. Calcd. for $C_{31}O_{23}OBr$: Br, 16.29. Found: Br, 16.03. *Anal.* of Methane. Calcd. for $C_{31}H_{23}Br$: Br, 16.84. Found: Br, 17.20. *Mol. wt.* in benzene. Calcd.: 475. Found: 497.

Rearrangement of *Sym.*-**3,3′-Dibromo-4″,4‴-Diphenylbenzopinacol.**—This rearrangement was carried out with 2 g. of pinacol in the same way as that of the 4,4′-dibromo-4″,4‴-diphenylbenzopinacol. The pinacolin gave only 0.002 g. of *m*-bromobenzoic acid, which is practically negligible. Thus the rearrangement is due entirely to the migration of the *p*-phenyl-phenyl group. The pinacolin, recrystallized from glacial acetic acid, melts at 202–203°.

Anal. Calcd. for $C_{38}H_{26}OBr_2$: Br, 24.32. Found: Br, 24.14. *Mol. wt.* in benzene. Calcd.: 658. Found: 652.

The constitution of the methane compound as 4,4′-diphenyl-3″-bromotriphenylmethane was verified by preparing it from the *m*-bromobenzoic ester exactly as was described for the *p*-bromomethane. The carbinol melted at 304° and the methane at 143°.

Anal. of Carbinol. Calcd. for $C_{31}H_{23}OBr$: Br, 16.29. Found: Br, 16.58. *Anal.* of Methane. Calcd. for $C_{31}H_{23}Br$: Br, 16.84. Found: Br, 16.70. *Mol. wt.* in benzene. Calcd.: 475. Found: 469.

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Summary

1. It has been shown that the method suggested by Gomberg and Bachmann can be applied to the preparation of many halogeno-benzopinacols, especially those from ketones containing bromine or chlorine atoms meta or para to the CO group. When the halogen atom is in the ortho position, however, the magnesium of the reducing mixture tends to remove the halogen atom from the ketone molecule and no pinacol is formed.

2. By a study of the iodomagnesium pinacolates from the point of view of Beer's law, the existence of the equilibrium pinacolate $\rightleftharpoons$ ketyl, has been demonstrated.

3. The relative migratory tendencies of the *p*-bromophenyl, *m*-bromophenyl and *p*-phenyl-phenyl groups have been determined by rearrangement of the appropriate pinacols to pinacolins. The results obtained are in good agreement with those obtained by previous investigators on different examples.

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

REDUCTION OF AROMATIC 1,2-DIKETONES BY THE BINARY SYSTEM MAGNESIUM IODIDE (OR BROMIDE) + MAGNESIUM

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Benzil is reduced by the binary system[2] to the unsaturated glycolate, iodomagnesium–stilbene–diolate, $C_6H_5(IMgO)C{=}C(OMgI)C_6H_5$, which when hydrolyzed gives benzoin. We have now extended this reaction to various benzils and find that it may be applied even to halogen-substituted diketones without danger of removing the halogen. Many of the reactions of the new unsaturated glycolates are analogous to those of the parent substance. More definite evidence, however, has now been obtained in regard to the reaction between the diketones and MgI_2 alone. It was reported that benzil liberates iodine from MgI_2, presumably in accordance with the reaction

$$RCOCOR + 2MgI_2 \rightleftharpoons R(IMgO)C{=}C(OMgI)R + I_2 \qquad (1)$$

About 5% of the calculated amount of iodine was found to be set free but most careful search failed to reveal benzoin in the hydrolyzed reaction product. Experience with substituted, more reactive, benzils here described has now definitely proved the correctness of that hypothesis.

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[1] The material here presented is part of a dissertation submitted by F. J. Van Natta to the Faculty of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1928.

[2] Gomberg and Bachmann, THIS JOURNAL, **49**, 2584 (1927).