Anal. Calcd. for $C_{16}H_{16}$: C, 92.25; H, 7.75; mol. wt., 208. Found: C, 92.16; H, 7.61; mol. wt., 226.

1,2,3,4-Dibenz-1,3-cycloöctadiene-6-ol (IX).—A solution of sodium borohydride (0.4 g.) in 15 ml. of methanol containing one drop of 10% sodium hydroxide solution was added to a stirred solution of the ketone VIII (2.00 g.) in 30 ml. of methanol. After the resulting solution had been stirred for 2 hours at room temperature, it was diluted with 200 ml. of water. The *p*H of the aqueous phase was adjusted to 5 by the addition of 10% sulfuric acid solution, and the alcohol IX was extracted with ether. The ethereal solution was washed with water, saturated sodium bicarbonate solution and saturated sodium chloride solution, and dried over Drierite. Crystallization from ligroin of the residue obtained on distillation of the ether afforded 1.73 g. (86%) of the alcohol IX as white needles, m.p. 95–97°. A portion recrystallized from ligroin had m.p. 96.5–97.5°.

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.71; H, 7.29.

Dehydration of 1,2,3,4-Dibenz-1,3-cycloöctadiene-6-ol.—The alcohol IX (1.54 g.) and boric acid (0.5 g.) were placed in a short-path distillation apparatus. The mixture was heated gradually to 270–275°, while the pressure was slowly reduced to 0.1 mm., and these conditions were maintained for 30 minutes. The distillate, which quickly solidified, was crystallized from 95% ethanol to give 0.771 g. (55%) of a mixture of the isomeric olefins Xa and Xb, m.p. 88–109°. Recrystallization did not narrow the melting range, nor did treatment of the mixture with sodium ethoxide in boiling ethanol for 18 hours give a single pure isomer.

Anal. Calcd. for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 93.10; H, 7.15.

A portion of the olefin mixture (0.117 g.) was hydrogenated at atmospheric pressure and room temperature in 15 ml. of glacial acetic acid in the presence of 0.4 g. of 10% palladium-on-carbon. After 30 minutes, 99% of one molar equivalent of hydrogen had been absorbed. The catalyst was removed by filtration, and the solvent was distilled under reduced pressure. The residue was sublimed at 120° (0.3 mm.) and crystallized from 95% ethanol to give 0.095 g. (81%) of the hydrocarbon II, m.p. 150–151.5°. After recrystallization from 95% ethanol the melting point was 150.5–151.1°. The infrared spectrum of the hydrogenation product was identical with that of an authentic sample of II obtained by Wolff–Kishner reduction of VIII and mixed melting point showed no depression.

1,2,3,4-Dibenz-1,3-cycloheptadiene (XI).—The ketone III (0.50 g.) and 85% hydrazine hydrate (2 ml.) were added to a solution of 1.0 g. of potassium hydroxide in 10 ml. of diethylene glycol. The mixture was heated under reflux for 2 hours, and then water and excess hydrazine were distilled until the temperature of the reaction mixture reached 200°. The distillate was extracted with ether, which was used later for extractions. The reaction mixture was heated under reflux at 200° for 3 hours, and then cooled and diluted with 80 ml. of water. After the mixture had been acidified with hydrochloric acid, it was extracted with ether, and the ethereal solution was washed with water, saturated sodium bicarbonate solution and saturated sodium chloride solution. The ether was distilled, and the residue was distilled in a short-path apparatus at 90–100° (0.1 mm.). The distillate solidified and was crystallized from methanol to give 0.235 g. (50%) of the hydrocarbon XI, m.p. 39.8–40.8°.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DE PAUL UNIVERSITY]

Pinacol Rearrangement of *sym-p,p'*-Dialkoxybenzopinacols

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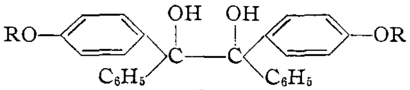
Four *sym-p,p'*-dialkoxybenzopinacols have been prepared by two bimolecular reduction procedures and subjected to the pinacol rearrangement. The migrational aptitudes of the *n*-propoxy-, *n*-butoxy-, *n*-amyloxy- and isoamyloxyphenyl groups all fall in the range 93–95%.

The migrational aptitudes of the *p*-methoxy- and the *p*-ethoxyphenyl groups are known to be very high in the pinacol rearrangement of *sym*-pinacols (I).[2,3] Similar results are now reported for four larger alkoxyl groups.



I

These benzopinacols were prepared by the bimolecular reduction of *p*-alkoxybenzophenones using as reducing agents both magnesium and iodine,[4] and zinc and acetic acid.[3,5] Both procedures were satisfactory, but the second was more convenient. The *p*-alkoxybenzophenones were prepared by benzoylating appropriate alkyl phenyl ethers[6] and more satisfactorily by alkylating *p*-hydroxybenzophenone.[7]

The pinacol rearrangement was done by boiling in acetic acid with a little iodine,[8] but the alkoxybenzopinacolones could not be separated. Therefore, the migrational aptitudes were determined according to Bailar's[8] procedure in which the pinacolones are not isolated, but are cleaved by alcoholic alkali to triarylmethanes and arylcarboxylic acids. The neutral equivalent of the acid permits calculation of the mole percentages of benzoic and *p*-alkoxybenzoic acids so formed and of the relative migrational aptitudes of the *p*-alkoxyphenyl group. The results (Table I) for all four alkoxyphenyls are comparable to the 98.3 and 98.6% previously reported for *p*-methoxy- and *p*-ethoxyphenyl.[2,3] We believe that the difference between our values

TABLE I

MIGRATIONAL APTITUDES OF *p*-ALKOXYPHENYL GROUPS

Alkoxy	Eq. wt. of acid mixt.	Migrational aptitude
Methoxy[2]		98.6
Ethoxy[3]		98.3
n-Propoxy	125.5	94.1
n-Butoxy	126.8	94.0
n-Amyloxy	127.0	95.1
i-Amyloxy	128.6	93.4

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[2] W. E. Bachmann and F. H. Moser, THIS JOURNAL, **54**, 1194 (1932).

[3] W. E. Bachmann and J. W. Ferguson, *ibid.*, **56**, 2081 (1934).

[4] M. Gomberg and W. E. Bachmann, *ibid.*, **49**, 251 (1927).

[5] P. J. Montagne, *Rec. trav. chim.*, **29**, 150 (1908).

[6] C. Torres, *Anales soc. españ. fis. y quim.*, **24**, 82 (1936); *C. A.*, **20**, 2158 (1926).

[7] Y. Bonnard and J. Meyer-Oulif, *Bull. soc. chim.*, **49**, 1303 (1931).

[8] J. C. Bailar, Jr., THIS JOURNAL, **52**, 3596 (1930).

TABLE II

sym-p,p'-DIALKOXYBENZOPINACOLS

Alkoxy	Method	Yield, %	M.p., °C.[a]	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
n-Propoxy	A	62	146–147	$C_{32}H_{34}O_4$	79.62	79.45	7.10	7.25
	B	78	145–146.5					
n-Butoxy	A	54	145.5–147	$C_{34}H_{38}O_4$	79.97	79.81	7.51	7.45
	B	62	146–147					
n-Amyloxy	A	42	119.5–121	$C_{36}H_{42}O_4$[b]	80.26	80.15	7.86	7.88
	B	42	120–121.5					
i-Amyloxy	A	52	127–128	$C_{36}H_{42}O_4$[b]	80.26	79.61	7.86	7.72
	B	35	127–129					

[a] Mixed melting points of the products of both methods were not depressed. [b] Analysis by Micro Tech Laboratories, Skokie, Ill.

and these is not significant since our results show that the size of the alkoxyl group does not materially affect migrational aptitudes.

Experimental[9]

***p*-Alkoxybenzophenones. A. From Alkyl Phenyl Ethers.**[6]—The alkyl phenyl ether[10] (0.24 mole) was added dropwise with stirring and cooling to 0.24 mole of benzoyl chloride and 0.30 of anhydrous aluminum chloride in 300 ml. of carbon disulfide. Temperatures were kept below 30°. The mixture was allowed to stand overnight before being hydrolyzed. The carbon disulfide layer was washed with 10% aqueous sodium hydroxide and with water, and the solvent was removed by distillation or evaporation. Crystallization of *p*-*n*-propoxybenzophenone from 200 ml. of ethanol gave a 59% yield, m.p. 62–63.5° (lit.[6] 65–66°). The *n*-butoxy compound was twice distilled to give a 60% yield of product, b.p. 210–219° (5 mm.), m.p. 34–36° (lit.[6] m.p. 38–39°). Two distillations gave 36% of *p*-*n*-amyloxybenzophenone, b.p. 211–212° (2 mm.), m.p. 35–36.5°.

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.51; H, 7.81.

B. From *p*-Hydroxybenzophenone.[7]—The alkyl iodides or bromides (0.075 mole) were boiled under reflux for nine hours with 0.063 mole of sodium ethoxide and 0.063 mole of *p*-hydroxybenzophenone in 35 ml. of absolute ethanol. The alcohol was distilled, water was added to the residue and the aqueous mixture was extracted into ether. The ether solution was washed successively with 10% aqueous sodium hydroxide, aqueous sodium bisulfite and then with water. Vacuum distillation isolated the product. In this way, there was obtained a 51% yield of *p*-*n*-amyloxybenzophenone, b.p. 210–211° (2 mm.), m.p. 34.5–36°. The yield of isoamyloxy analog was 56%, b.p. 209–210° (2 mm.) (lit.[6] 225–240° (15 mm.)).

***sym.*-*p,p'*-Dialkoxybenzopinacols. A. By Reduction with Magnesium and Iodine.**[4]—Magnesium turnings (0.21 g. atom), 33 ml. of dry ether and 50 ml. of dry benzene were placed in a 250-ml. pressure bottle fitted with a reflux condenser. To this, 0.11 mole of iodine was added portionwise at a rate that maintained a vigorous reaction. Occasionally, initial heating was necessary to start it. When the solution was almost colorless, it was cooled, the condenser was removed and 0.10 mole of *p*-alkoxybenzopinacol was added. The bottle was immediately stoppered and shaken in a shaking machine for one hour. During this period an exothermic reaction caused color changes from colorless to reddish-brown to colorless to deep red. The solution was decanted into cold water which was then carefully treated with hydrochloric acid to dissolve the magnesium hydroxide. The ether layer was washed with sodium bisulfite solution, dried and evaporated. Finally, crystallization from a minimum amount of ethanol gave the *sym-p,p'*-dialkoxybenzopinacol (Table II).

B. By Reduction with Zinc and Acetic Acid.[2]—A mixture of 0.01 mole of *p*-alkoxybenzophenone, 5 g. of powdered zinc and 30 ml. of acetic acid was kept at room temperature for six days after which it was diluted with water and extracted with ether. The ether extract was washed with aqueous sodium carbonate and with water before being dried and evaporated. Crystallization from ethanol gave the product (Table II).

Migration Aptitudes.[8]—A 3.0-g. sample of the pure pinacol was boiled for one hour in 30 ml. of glacial acetic acid with a small crystal of iodine. It was then poured into 400 ml. of water containing a little sodium bisulfite, and the gummy precipitate was separated, washed with water and dried. All the dried material was cleaved by boiling for 12 hours with 2% alcoholic potassium hydroxide. This alcoholic solution was poured into water and the mixture was partly evaporated until the non-soluble materials coagulated and could be removed. The aqueous solution of potassium benzoate and *p*-alkoxybenzoate was extracted once with ether and acidified and the precipitated mixture of acids was dried in a vacuum desiccator. Titration with standard alkali permitted calculation of the equivalent weight of the mixed acid (Table I), amount of benzoic acid present, the mole percentages of benzoic and *p*-alkoxybenzoic acids and the migrational aptitude (100 minus the mole per cent. *p*-alkoxybenzoic acid) of the *p*-alkoxyphenyl group.

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(9) All melting and boiling points are uncorrected.

(10) Prepared in 66–79% yield according to the directions for phenetole; W. J. Hickinbottom, "Reactions of Organic Compounds," 2nd ed., Longmans, Green and Co., London, 1948, p. 91.