Anal. Calcd. for $C_{18}H_{24}O_4N_2S$: N, 7.69; S, 8.79. Found: N, 7.56; S, 8.74, 8.66.

This dehydrated compound was also produced by heating 5 g. of *p*-aminoacetanilide-*d*-camphor-10-sulfonate to 220° for about thirty minutes. This compound also melted at 375–380° (bloc Maquenne).

Anal. Calcd. for $C_{18}H_{24}O_4N_2S$: N, 7.69; S, 8.79. Found: N, 7.87; S, 8.74.

Dehydration of Aniline-*d*-camphor-10-sulfonate.—A weighed sample of the aniline salt was heated in an oven at 200° for three hours. This material was then weighed again and found to have lost weight equivalent to one mole of water. Calcd.: 5.54%. Found: 5.70%.

This anil was then dissolved in chloroform, treated with norite several times to decolorize, and the anil precipitated by adding petroleum ether to the boiling chloroform solution. The yield was 76 g., or 87% of the theoretical value; m. p. 294–295° (bloc Maquenne).

Anal. Calcd. for $C_{16}H_{21}O_3NS$: N, 4.56; S, 10.42. Found: N, 4.59; S, 10.25.

A neutral equivalent was determined for this anil whose calculated molecular weight was 307; found, 306.3.

The original aniline salt may also be titrated. The calculated molecular weight is 325; found, 322.3.

The rotations of the anil were determined in the same solvents as the aniline salt for comparative purposes. It will be noted that, in the same solvent, both reached the same equilibrium point (see Fig. 2).

Summary

The salts of *d*-camphor-10-sulfonic acid and primary amines exhibit slow mutarotation in anhydrous solvents.

The salts aniline-*d*-camphor-10-sulfonate and *p*-aminoacetanilide-*d*-camphor-10-sulfonate, which are *dextro*rotatory, have been dehydrated, leading to the formation of *levo*rotatory compounds which have been characterized as anils.

The mutarotation phenomenon hence appears to be due to the establishment of an equilibrium between the *d*-salt and the *l*-anil.

URBANA, ILLINOIS RECEIVED MAY 3, 1935

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

Hexa-*p*-alkylphenylethanes. The Effect of the *p*-Alkyl Group on the Dissociation of the Ethane

BY J. W. COPENHAVER, MAX F. ROY AND C. S. MARVEL

The observation[1] that increasing the size of the alkyl groups from *t*-butyl to *t*-hexyl in a hexaalkylethinylethane definitely weakened the central ethane linkage led us to believe that the weight of the attached groups may have an important role in the dissociation of other ethanes into free radicals. In order to put this theory to test, we have undertaken the present study of hexa-*p*-alkylphenylethanes.

Saturated alkyl groups were used in order to avoid, as far as possible, any significant change in the unsaturated character of the aryl group. The *p*-alkyl group was used in order to introduce the least amount of steric hindrance effect. Moreover, it was felt that a series of *p*-alkylaryl groups differing by one methylene group would differ very little in any property save weight.

In this communication we describe the preparation of a series of hexa-*p*-alkylphenylethanes in which the alkyl group varies from ethyl to butyl. The ethanes were prepared by treating the triarylchloromethanes with molecular silver as described by Gomberg.[2] The chlorides were synthesized by the usual reactions. The chief difficulties in the synthetic work came in connection with the preparation of the necessary *p*-bromoalkylbenzenes and in the crystallization of the tri-*p*-alkylphenylchloromethanes.

The *p*-bromoalkylbenzenes were prepared by several reactions. Treatment of *p*-bromophenylmagnesium bromide with two moles of an alkyl sulfate or *p*-toluenesulfonate gave about a 40–60% yield of bromoalkylbenzene. *p*-Bromoethylbenzene was most readily prepared from ethyl sulfate by this method. *p*-Bromo-*n*-propylbenzene and *p*-bromoisobutylbenzene were more easily prepared by treating *p*-bromophenylmagnesium bromide with allyl bromide and methylallyl chloride followed by reduction of the unsaturated derivatives. *p*-Bromoisopropylbenzene, *p*-bromo-*s*-butylbenzene and *p*-bromo-*n*-butylbenzene were most readily prepared by condensing *p*-bromophenylmagnesium bromide with acetone, ethyl methyl ketone and *n*-butyraldehyde followed by dehydration of the carbinols and reduction of the resulting unsaturated hydrocarbons.

---

(1) Davis and Marvel, THIS JOURNAL, **53**, 3840 (1931).

(2) Gomberg and Cone, *Ber.*, **37**, 1626 (1904); **39**, 3286 (1906).

The tri-*p*-alkylarylcarbinols were prepared from the Grignard reagents of the *p*-bromoalkylbenzenes and diethyl carbonate.[3] None of the carbinols could be obtained in crystalline form, and they decomposed on attempted distillation. They were, therefore, converted to the corresponding chlorides which could be crystallized. The hexa-*p*-alkylphenylethanes in which the alkyl groups were ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl and *s*-butyl were prepared in toluene solution from 0.001 mole of the chloride. Hexaphenylethane and hexa-*p*-tolylethane were prepared similarly for comparison.

The solution of the hexaphenylethane was a light yellow and that of the hexa-*p*-tolylethane light reddish-orange as previously described.[4] The solution of the *p*-ethylphenyl derivative was a deeper reddish-orange and solutions of the *n*-propyl, isopropyl, *n*-butyl and *s*-butyl derivatives were distinctly red in color. Solutions of the branched-chain alkyl derivatives were slightly deeper in color than were the straight-chain derivatives. The *n*-propyl derivative seemed to be darker than either the ethyl or *n*-butyl derivative, but the color was not sufficiently different to be certain of this point. That the colors of these solutions were due to the presence of free radicals in solution was demonstrated by the fact that the color disappeared quickly when air was admitted to the tubes containing the solutions, and the corresponding peroxide was obtained in each case. Moreover, the more deeply colored solutions faded to a light yellow color when they were cooled to a low temperature.

It is generally assumed that the depth of color of a solution of a hexaarylethane is a qualitative measure of its degree of dissociation. An example of this rule is furnished by the work of Schlenk, Weickel and Herzenstein[5] on the series of compounds from the slightly dissociated hexaphenylethane to the completely dissociated hexabiphenylethane in which the color varies from light yellow to deep violet or black. The observations reported above furnish evidence that increasing the weight of the aryl group by introducing various alkyl groups in the *para* position does cause an increase in the dissociation of a hexaarylethane. However, accurate measurements on the degree of dissociation of these new ethanes are needed before the theoretical significance of this work can be completely evaluated.

Experimental

Preparation of *p*-Bromoalkylbenzenes

Method A.—From *p*-bromophenylmagnesium bromide and alkyl *p*-toluenesulfonates.

p-Bromophenylmagnesium bromide was prepared according to the directions of Quelet[6] excepting that a mixture of 250 cc. of benzene and 400 cc. of dry ether per mole of *p*-dibromobenzene was used as a solvent for the reaction.

The reactions between this Grignard reagent (1 mole) and the various alkyl *p*-toluenesulfonate (2 moles) were carried out in the manner described by Marvel and Rossander[7] for similar reactions, excepting that the mixtures were heated for twelve to sixteen hours instead of eight hours.

p-Bromoethylbenzene was prepared from *p*-bromophenylmagnesium bromide and diethyl sulfate according to the method used by Gilman and Catlin[8] for *n*-propylbenzene. With two moles of the sulfate per mole of *p*-bromophenylmagnesium bromide, the yield was 57% of the theoretical amount.

The *p*-bromoalkylbenzenes were distilled through a Widmer column to remove traces of *p*-dibromobenzene.

Method B.—By Reduction of *p*-Bromoalkylenebenzenes. *p*-Bromoallylbenzene was prepared by the method of Quelet[9] in a yield of 68.5% of the theoretical amount.

Similarly, 2-methyl-3-*p*-bromophenylpropene was made from *p*-bromophenylmagnesium bromide (2 moles) and β-methylallyl chloride (2.2 moles). The yield was 64.5% of the theoretical and the compound had the following properties: b. p. 98° (5 mm.); n^{20}_{D} 1.5573; d^{20}_{4} 1.3037. Calcd. for $C_{10}H_{11}Br$: Br, 37.88. Found: Br, 38.19.

p-Bromoisopropenylbenzene was prepared according to the method of Ziegler and Tiemann[10] from *p*-bromophenylmagnesium bromide and acetone. In our experiment it was not found necessary to use potassium acid sulfate to dehydrate the carbinol as this reaction occurred during isolation of the product.

By the same method 2-*p*-bromophenylbutene-2 was prepared from *p*-bromophenylmagnesium bromide (2 moles) and methyl ethyl ketone (2 moles). The yield was 74% of the theoretical amount of a product boiling at 111° (6 mm.), n^{20}_{D} 1.5792, d^{20}_{4} 1.3223. Calcd. for $C_{10}H_{11}Br$: Br, 37.88. Found: Br, 38.12.

1-*p*-Bromophenylbutene-1 was prepared by the method of Quelet[9] from *p*-bromophenylpropylcarbinol.

These *p*-bromoalkylenebenzenes were reduced with hydrogen and platinum in alcoholic solution according to the method of Adams, Voorhees and Shriner[11] to give the *p*-bromoalkylbenzenes. The results of these experiments are collected in Table I.

Tri-*p*-alkylphenylcarbinols.—The triarylcarbinols were prepared from the *p*-bromoalkylbenzenes by converting

---

[3] Moyer and Marvel, "Organic Syntheses," John Wiley and Sons, New York, 1931, Vol. XI, p. 98.

[4] Gomberg, *Ber.*, **37**, 1626 (1904).

[5] Schlenk, Weickel and Herzenstein, *Ann.*, **372**, 1 (1910).

[6] Quelet, *Bull. soc. chim.*, **41**, 933 (1927).

[7] Marvel and Rossander, THIS JOURNAL, **50**, 1491 (1928).

[8] Gilman and Catlin, "Organic Syntheses," John Wiley and Sons, New York, 1932, Coll. Vol. I, p. 458.

[9] Quelet, *Bull. soc. chim.*, **45**, 75 (1929).

[10] Ziegler and Tiemann, *Ber.*, **55**, 3415 (1922).

[11] Adams, Voorhees and Shriner, "Organic Syntheses," John Wiley and Sons, New York, 1932, Coll. Vol. I, pp. 53, 452.

TABLE I

p-BROMOALKYLBENZENES[a]

Alkyl group	B. p., °C.	Mm.	Method	Yield, %	n^{20}_D	d^{20}_4	Analysis for Br Calcd.	Found
C_2H_5	95–96	20	A	40	1.5462	1.3478	43.12	43.19
n-C_3H_7	85–86	4	A	43	1.5320	1.2830	40.15	40.38
i-C_3H_7	97–98	5	B	87	1.5569	1.3145	40.15	39.99
n-C_4H_9	102	6	A	42				
			B	90	1.5388	1.2347	37.52	37.37
i-C_4H_9	97–98	5	B	87	1.5331	1.2609	37.52	37.13
s-C_4H_9	94	4	B	85	1.5340	1.2605	37.52	37.91
n-C_5H_{11}	109–110	4	A	41	1.5237	1.2038	35.21	35.22

[a] All of the compounds listed in Table I have been reported previously in the literature, but only very meager accounts of their physical constants are to be found.

them to Grignard reagents and treating with diethyl carbonate.[3] Since the care with which this reaction was carried out determined whether or not a pure crystalline chloride could be obtained, it seems advisable to give the details of the procedure.

In a 1-liter, 3-necked flask fitted with a stirrer, separatory funnel and a reflux condenser was placed 12.15 g. (0.5 mole) of magnesium and then a few cc. of a solution of 0.5 mole of the *p*-bromoalkylbenzene in 300 cc. of dry ether was introduced. The reaction was started by adding a few drops of ethylmagnesium bromide solution. When the reaction had set in, the rest of the ether solution of the *p*-bromoalkylbenzene was added at such a rate that the ether boiled gently. The ether solution was boiled for about a half hour after the addition of all of the halide. A solution of 14.75 g. (0.125 mole) of diethyl carbonate in 100 cc. of dry ether was then added over a period of several hours. It was very important that the Grignard reagent was always in excess since otherwise the carbinols seemed to contain esters and ketones which prevented crystallization of the chlorides in the next reaction. The amount of diethyl carbonate used was less than that calculated on the basis of a 75% yield of Grignard reagent. Toward the end of the addition of the diethyl carbonate, the reaction mixture was tested for Grignard reagent[12] and if this test became negative no further diethyl carbonate was added. In nearly every experiment the amount mentioned above could be used.

The reaction mixture was stirred overnight and then decomposed with an ice-cold solution of ammonium chloride in water. The ether layer was separated and the water extracted twice with a little ether. The combined ether solutions were distilled to remove the solvent and the residue was distilled with steam until no more water-insoluble material passed over with the steam. After cooling, the carbinol was again taken up in ether, the solution dried over magnesium sulfate, filtered and the solvent removed to leave the crude carbinol.

The tri-*p*-alkylphenylcarbinols, where the alkyl group was ethyl, *n*-propyl. isopropyl, *n*-butyl, isobutyl, *s*-butyl, and *n*-amyl were prepared in this manner. The crude yields were 90–95%, based on the diethyl carbonate used. All were straw-colored oils which became viscous on cooling, but did not crystallize. Analyses for carbon and hydrogen indicated that they were essentially pure and they were converted to the chlorides without further purification.

Tri-*p*-alkylphenylchloromethanes.—The procedure of Gomberg[13] was followed in making the chlorides. A solution of 0.1 mole of the crude carbinol in 200 cc. of dry ether was treated with dry hydrogen chloride in the presence of 10 g. of anhydrous calcium chloride. Hydrogen chloride was passed into the solution until it was thoroughly saturated, and the color changed to dark brown. After about thirty minutes the solution was filtered to remove the calcium chloride and the ether was removed under reduced pressure until the remaining volume was about 60–75 cc. The solution was then placed in a stoppered Erlenmeyer flask and cooled in an ice–salt bath. After some time, the chloride separated as slightly brownish crystals. When no more crystals seemed to separate, the solution was filtered on a Buchner funnel and the crystals were washed with cold (0°) low-boiling petroleum ether. By concentration of the mother liquors and further cooling, a second crop of crystals could sometimes be obtained. The yield of crude chloride was usually 75–85%. The pure chlorides were obtained by recrystallization of the brownish products from dry ethyl acetate. The products had to be protected even from moisture in the air to avoid decomposition. The properties of the new compounds are listed in Table II.

TABLE II

TRI-*p*-ALKYLPHENYLCHLOROMETHANES

Alkyl groups	M. p., °C.	Analysis for Cl Calcd.	Found
C_2H_5	157–158	9.78	9.71; 9.77
n-C_3H_7	88–89	8.76	8.62; 8.69
i-C_3H_7	167–168	8.76	8.43; 8.53
n-C_4H_9	63	7.94	7.89; 7.91
i-C_4H_9	135–136	7.94	7.76; 7.83
s-C_4H_9	132–133	7.94	7.99; 8.10

The tri-*p*-*n*-amylphenylcarbinol did not give a crystalline chloride.

Hexa-*p*-alkylphenylethanes.—The ethanes were prepared by placing 0.001 of a mole of each of the above tri-*p*-alkylphenylchloromethanes in a Pyrex test-tube and adding 0.4 g. of molecular silver and 10 cc. of dry toluene. The test-tube was then evacuated until the toluene vapors had replaced the air and sealed. The tubes were shaken for about forty-eight hours, and the precipitate of silver and silver chloride was allowed to settle. The solutions were protected from direct sunlight. For comparison, solutions of hexaphenylethane (light yellow) and hexa-*p*-tolylethane (light reddish-orange) were prepared in a similar manner. Hexa-*p*-ethylphenylethane gave a somewhat deeper reddish-orange solution. The two propyl and the three butyl derivatives gave solutions that were distinctly red with slight variations in shade. The *n*-propyl derivative was slightly lighter than the isopropyl. Also, the *n*-butyl derivative was less deeply colored than either of the propyl derivatives or the branched-chain butyl derivatives.

Cooling the tubes containing these deeply colored solutions by dipping them in an acetone–carbon dioxide bath caused the colors to fade, but in no case did the color completely disappear. The original color returned when the solutions were allowed to warm up to room tempera-

---

(12) Gilman and Schulze, THIS JOURNAL, **47**, 2002 (1925).

(13) Tousley and Gomberg, *ibid.*, **26**, 1516 (1904).

ture. After standing for a few weeks, the colors had faded only slightly.

Tri-*p*-alkylphenylmethyl Peroxides.—The ethanes (or free radicals) were characterized by their corresponding peroxides. The peroxides were prepared by allowing the solutions of the ethanes to stand in the presence of the oxygen in the air. The color of the solutions was quickly discharged and after the silver–silver chloride mixture had been filtered off, the solvent was evaporated. The residue was taken up in as little benzene as possible, and five to ten times the volume of absolute alcohol was added. The white crystalline peroxides precipitated out on standing, and were recrystallized by the same process.

The melting points and analyses of the peroxides are given in Table III.

TABLE III

TRI-*p*-ALKYLPHENYLMETHYL PEROXIDES

Alkyl group	M. p., °C.	Analysis, % Calculated C	H	Found C	H
C_2H_5	159–160	87.42	7.93	87.03	7.99
n-C_3H_7	140–141	87.22	8.63	87.08	8.63
i-C_3H_7	162–163	87.22	8.63	86.79	8.71
n-C_4H_9	127–128	87.02	9.20	86.75	9.30
i-C_4H_9	135–136	87.02	9.20	87.08	9.23
s-C_4H_9	147–148	87.02	9.20	86.95	9.28

Summary

A series of hexa-*p*-alkylphenylethanes in which the alkyl group was ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl and *s*-butyl has been prepared. The color of equimolar solutions of these ethanes becomes deeper as the weight of the alkyl group is increased.

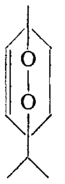
URBANA, ILLINOIS RECEIVED MAY 6, 1935

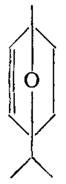
[CONTRIBUTION FROM THE LABORATORY OF DR. D. JAYNE AND SON, INC.]

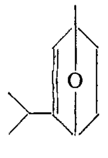
Dehydrocineoles. I. The Preparation of 2-Isopropyl-5-methylfuran and its Condensation with Maleic Anhydride

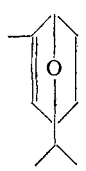
BY LEWIS W. BUTZ

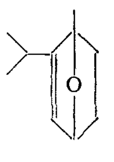
Compounds related to ascaridole (I) but lacking the peroxide group were desired. The dehydrocineoles (II-VII) are so related. Derivatives of these and of the related cineoles and menthadienes should be accessible through application of the reactions studied by Diels and Alder[1] to the isopropylmethylfurans.

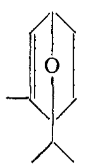

I

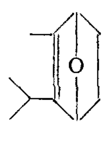

II


III


IV


V


VI


VII

None of the six possible isopropylmethylfurans has previously been prepared. 2-Isopropyl-5-methylfuran has now been obtained in 40% yield by the dehydration of 2-methylheptane-3,6-dione with sulfuric acid. This method seems not to have been employed previously with unsubstituted aliphatic 1,4-dicarbonyl compounds. Furan derivatives have been obtained by the action of concentrated sulfuric acid and other acid reagents on arylated, carbalkoxylated and other substituted 1,4-dicarbonyl compounds. Willstätter and Clarke[2] obtained a small quantity of tetramethylfuran from α,β-diacetylbutyric ester by treatment with methyl iodide, sodium ethoxide and dilute sulfuric acid. Harries[3] obtained furan by heating succinaldehyde to 180°. Dietrich and Paal[4] made 2,5-dimethylfuran in 25% yield from acetonylacetone and zinc chloride.

The 2-isopropyl-5-methylfuran reported here is a colorless liquid with an odor somewhat similar to that of toluene. It has the following constants: b. p. (770 mm.) 135–137°; $d^{20}{}_4$ 0.8932; $n^{23}{}_D$ 1.4429. This furan gives a violet color in the pine shaving test as carried out by Reichstein,[5] and condenses with maleic anhydride to give a solid melting at 77°. Elementary analysis and titration with sodium hydroxide in water indicate the structure IX. The structure VIII is provisionally assigned to the furan although it cannot at present be stated with certainty that the product is free from isomers containing olefin linkages in

---

[1] Diels and Alder, *Ber.*, **62**, 554 (1929); *Ann.*, **490**, 243 (1931).

[2] Willstätter and Clarke, *Ber.*, **47**, 308 (1914).

[3] Harries, *ibid.*, **34**, 1496 (1901).

[4] Dietrich and Paal, *ibid.*, **20**, 1085 (1887).

[5] Reichstein, *Helv. Chim. Acta*, **15**, 1112 (1932).