to calculate a σ-value for the *m*-phenyl group by means of Hammett's equation.[5] The data are summarized in Table I.

TABLE I

APPARENT IONIZATION CONSTANTS IN 50% AQUEOUS BUTYL CELLOSOLVE AT 25° AND IONIC STRENGTH 0.05

Acid	pK_A	No. of determinations
Benzoic[a]	5.66 ± 0.024	5
m-Phenylbenzoic	5.58 ± 0.018	4

[a] Berliner and Blommers[3] give pK_A = 5.65 ± 0.01 for this compound.

The resulting σ-value is +0.06 ± 0.03. Interpretation of this result is simpler than for the triphenylchloromethanes. No steric factors can be involved. The absence of any complexing or specific interaction of the solvent with the *m*-phenyl group can be deduced from the fact[6] that the ultraviolet spectrum of benzene in solution in water, ethanol or diethyl ether, resembles its spectrum in the gas phase even more closely than does its spectrum in cyclohexane solution, the differences in all these cases being very small. It is not possible, however, to distinguish between the remaining two possibilities. The results can readily be explained in terms of phenyl having a small fundamental electron attracting influence relative to hydrogen. The possibility that resonance interaction between the two phenyl groups is reduced by the presence of a positive charge in one of them is also in accord with the facts. Symbolic structures in which such a charge is distributed to the ortho and para positions of the disubstituted ring are more important in the un-ionized acid than in the anion and might lead to a greater decrease in interaction of the benzene rings and a consequent small destabilization of the acid.

Experimental

Materials.—The benzoic acid was National Bureau of Standards Acidimetric and Calorimetric Standard No. 39-f. The *m*-phenylbenzoic acid was prepared by carboxylation of the corresponding Grignard reagent. Eastman Kodak Co. Practical *o*-aminobiphenyl was converted to *m*-bromobiphenyl by the method of Huber, *et al.*,[7] modified by deaminating with hypophosphorous acid[8] instead of ethanol and copper bronze. A 42.5% over-all yield of bromide with $n^{24}D$ 1.6394 and a b.p. of 104° at 0.2 mm. was obtained.

This compound was converted to the Grignard reagent by reacting with Dow Corporation "Super Pure" magnesium.[9] The reaction proceeded very slowly in dry ether (at 1 molar concn.) and was accompanied by formation of a white precipitate. On addition of about 7% by volume of dry benzene the precipitate dissolved and the reaction proceeded smoothly. Hydrolysis and acid titration of an aliquot indicated a 94% yield after one hour. The product obtained after treating the Grignard solution with gaseous CO_2 dried by passage through concentrated sulfuric acid was recrystallized four times from hot approximately 50% aqueous ethanol to give a 44% yield of purified material, m.p. 165.4–166.0°.[10]

Howe and French Co. technical grade butyl cellosolve was purified by the method of Halford[11] to yield material boiling at 106–107° at 70 mm. pressure.

Measurements.—The pK_A values were determined with essentially the same procedures and conditions as those of Berliner and Blommers.[3] The temperature was 25.10 ± 0.25°. Each sample was maintained under a nitrogen atmosphere throughout its titration. A Leeds and Northrup No. 7662 *p*H meter and glass electrode sensitive to ±0.01 *p*H unit were employed. Asymmetry of the glass electrode was corrected using Coleman Certified buffer tablets of *p*H 4.00, 5.00, 6.80 and 7.00. Individual pK_A values were 5.70, 5.68, 5.65, 5.64, 5.63 for benzoic acid and 5.57, 5.57, 5.61, 5.56 for *m*-phenylbenzoic acid.

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Phenol Alcohols in the Ammonia-Catalyzed Phenol–Formaldehyde Reaction

BY R. W. MARTIN

RECEIVED MARCH 6, 1952

It has been shown that di- and tri-(hydroxybenzyl)-amines are formed on heating phenols with hexamethylenetetraamine.[1–4] It is possible that similar amines are formed in phenol–aldehyde resins where ammonia has been used as catalyst. As the quantity of ammonia normally employed in preparing these resins is not sufficient to give amine derivatives with all the phenol and formaldehyde present other reactive intermediates must also be formed. The most logical products, in addition to the hydroxybenzylamines, are the mono- and polynuclear phenol alcohols. However, because of the rapid loss of water solubility in ammonia-catalyzed phenol–formaldehyde resins, the formation of phenol alcohols has been much debated.[4,5]

It has now been shown that at least at room temperature both phenol monoalcohols and phenol dialcohols may be separated from ammonia-catalyzed phenol–formaldehyde reaction products. The phenol alcohols, *p*-hydroxybenzyl alcohol and 2,4-di-(hydroxymethyl)-phenol, were separated from the phenol–formaldehyde reaction mixture according to a procedure previously described by Martin.[6]

Experimental

Phenol, 282 g. (3 moles), 362 g. of 37.2% formalin (4.5 moles) and 14.1 g. of 28% ammonia were mixed and held at 25–30° for 6 days. The reaction mixture was then dehydrated, treated with trimethylchlorosilane and the trimethylsilyl derivatives (662 g.) separated into twelve fractions by fractional distillation according to the procedure previously described.[6] Hydrolysis of Fraction III (b.p. 117–121° (1–2 mm.); weight, 104 g.) gave *p*-hydroxybenzyl alcohol and of Fraction VII (b.p. 106–121° (0.2–0.3 mm.); weight, 47.4 g.) gave 2,4-di-(hydroxymethyl)-phenol.

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The identity of the compounds was established by infrared absorption data and by mixed melting points with authentic samples of the materials. The nature of the nitrogen containing products was not investigated.

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The Ultraviolet Absorption Spectra of Some Terpene Hydrocarbons

BY ROBERT D. WALKER, JR., AND J. ERSKINE HAWKINS

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The use of ultraviolet absorption spectra in the chemistry of the terpenes was suggested about 1910 in a series of papers by Hantzsch[1] and Auwers.[2] These authors reported the ultraviolet absorption of a few terpenes but little interest was shown in the subject for a number of years. More recently there has been a renewal of interest in the ultraviolet absorption spectra of terpenes and several have been reported.[3-5] A relatively limited number of terpenes have been thus investigated, however, and it has seemed desirable to report the ultraviolet absorption spectra of some hydrocarbon terpenes which were available.

Experimental

The quantity of each sample used was determined by transferring an amount to a weighed volumetric flask partially filled with isoöctane and then reweighing. The flask was then filled to the 10-ml. mark with isoöctane and the solution thoroughly mixed. Successive 1:10 dilutions were made by transferring 1-ml. samples to 10-ml. volumetric flasks which were partially filled with isoöctane and then filling to the mark. Appropriate dilutions were made to give maximum optical densities of 0.4–0.9.

The spectra were measured with a Beckman spectrophotometer, using spectroscopic grade isoöctane (Phillips Petroleum Company) both as solvent and as standard.

Myrcene.—Myrcene was prepared by pyrolysis of β-pinene in the vapor phase at 465°.[6] The pyrolysate was fractionated at reduced pressure to obtain myrcene which had a refractive index, $n^{25}\text{D}$ of 1.4683. Simonsen[7] gives for this compound $n^{19}\text{D}$ 1.4700.

Ocimene.—The sample used in this investigation was prepared by vapor phase thermal isomerization of α-pinene and subsequent fractionation.[8] It had a refractive index $n^{25}\text{D}$ 1.4831. Enklaar[9] reported for ocimene $n^{18}\text{D}$ 1.4857.

Alloöcimene.—This compound was prepared by liquid phase thermal isomerization of α-pinene[10] and fractionation at reduced pressure. It had a refractive index $n^{25}\text{D}$ 1.5418 as compared to the value $n^{20}\text{D}$ 1.5446 reported by Simonsen[7] for the pure compound.

Alloöcimene Dimer.—Alloöcimene dimer was recovered by fractional distillation at reduced pressure of the mixture resulting from the liquid phase thermal isomerization of α-pinene. The sample used in this investigation had a refractive index $n^{25}\text{D}$ 1.5180. Fuguitt and Hawkins[10] found for this substance $n^{25}\text{D}$ 1.5171–82.

Results and Discussion

In Fig. 1 is shown the ultraviolet absorption curve of myrcene: λ_{max} 224.5 mμ; ϵ_{max} 15,350. Two very interesting subsidiary absorption bands appear as shoulders on the main absorption band with maxima at approximately 280 and 320 mμ. The band at 280 mμ may most probably be attributed to the presence of a small amount of alloöcimene (see Fig. 2). This compound would result from the thermal isomerization of any trace of α-pinene remaining in the β-pinene from which the myrcene was prepared by pyrolysis.[4,6] The substance responsible for the absorption at 320 mμ seems to be present in only trace quantities, and it does not now seem possible to attribute this absorption band to any known compound. It may be of some importance, however, to note that absorption in this region appears in the pyrolysis products of α- or β-pinene, but not in the absorption of the parent substances.

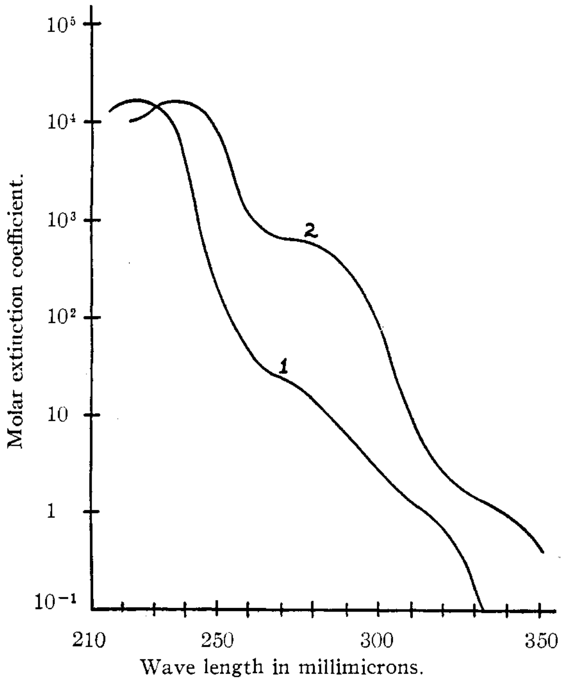

Fig. 1.—Ultraviolet absorption spectra in isoöctane at about 30°: 1, myrcene; 2, ocimene.

Also shown in Fig. 1 is the ultraviolet absorption of ocimene, 2,6-dimethyl-$\Delta^{1:5:7}$-octatriene; λ_{max} is 237 mμ and ϵ_{max} 16,400. The presence of approximately 2% of alloöcimene is indicated by the very prominent subsidiary band at 270–280 mμ. This can be accounted for by the relations between α-pinene, ocimene and alloöcimene.[8] Traces of the constituent absorbing at 320 mμ are also noted as in myrcene.

The ultraviolet absorption of alloöcimene, 2,6-dimethyl-$\Delta^{2,4,6}$-octatriene, is shown in Fig. 2. Alloöcimene shows three absorption peaks at 268, 277 and 288 mμ, ϵ_{max} being greatest (41,900) at 277 mμ. On the short wave length side of the broad triply-peaked maximum of alloöcimene there appear several inconspicuous shoulders. These may indicate hindered transitions in the alloöcimene mole-

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