The *erythro*-hydrochloride had a m.p. of 255–256°.

Anal. Calcd. for $C_{10}H_{20}ClNO$: C, 69.17; H, 7.26. Found: C, 69.30; H, 7.25.

The m.p. 100–101° was found for the *threo* isomer after purification by sublimation.

Determination of Yields of *erythro* and *threo* Isomers in the Synthesis of 1-Phenyl-1-*p*-tolyl-2-aminopropanol.—Carbonyl-labeled propiophenone-C^{14}, prepared by the Friedel–Crafts synthesis from propionic-1-C^{14} acid and benzene, was converted through the isonitroso derivative to the stannic chloride complex of 2-aminopropiophenone as described above. After the salt (15.1 g., 0.0502 mole) was dried and finely powdered, it was added in small portions to the Grignard reagent prepared from 85.5 g. of *p*-bromobenzene and 12.2 g. of magnesium. The mixture was heated at reflux temperature for 1 hr. and then hydrolyzed with ammonium chloride solution. The ether layer was removed and the aqueous layer was washed three times with 100-ml. portions of ether. The combined ether extracts were filtered and the ether was removed by evaporation. The organic material was quantitatively transferred to a 250-ml. volumetric flask and diluted to the mark with benzene. Two 50-ml. aliquots were removed with a pipet. From the remaining 150 ml. of benzene solution there was isolated about 5 g. of crude *erythro* compound. This was crystallized three times from hexane and sublimed; m.p. 86–87°, 2.734 mc. of carbon-14 mole.

One 50-ml. aliquot was added to 2.000 g. of pure non-radioactive *erythro* isomer which was then reisolated and crystallized three times from hexane (Norite) and sublimed; m.p. 86–87°, 1.252 mc. of carbon-14/mole. The yield was 70.0%. The other 50-ml. aliquot was added to 2.000 g. of pure non-radioactive *threo* isomer which was then reisolated, crystallized four times from hexane (Norite) and sublimed. To the sublimed *threo* isomer (0.5 g.) was added 30 mg. of pure non-radioactive *erythro* isomer. The mixture of compounds was crystallized twice from hexane and again sublimed; m.p. 100–101°, 0.02615 mc. of carbon-14/mole. The yield of *threo*-1-phenyl-1-*p*-tolyl-2-aminopropanol was therefore 0.8%.

Synthesis of 1,1,2-Triphenyl-2-aminoethanol-C^{14} (VIII).—The chain-labeled amino alcohol VIIIa was synthesized by the action of excess phenylmagnesium bromide on ethyl phenylaminoacetate-1-C^{14} hydrochloride[12]; m.p. 153.5–155°,[13] 2.158 mc. of carbon-14/mole. Phenyl-labeled amino alcohol VIIIc was synthesized by the action of phenyl-C^{14}-magnesium bromide upon aminodesoxybenzoin hydrochloride; m.p. 153–154°, 0.8883 mc. of carbon-14/mole.

Deamination of VIIIa and VIIIc.—The amino alcohol (250 mg.) was dissolved in 20 ml. of 50% aqueous acetic acid, and the solution was cooled in an ice–salt-bath. To this cold solution was added a solution of 179 mg. of sodium nitrite in 3 ml. of water dropwise while stirring over a period of 1 hr. The mixture was allowed to warm to room temperature and stirring was continued overnight. The solid phenyldesoxybenzoin which formed was removed by filtration and was then crystallized from ethanol (68% yield after purification); m.p. 135–136°.[14]

Radiochemical Structure Determination of VIIIa, VIIIc and Their Deamination Products, IXa and IXcd.—The position of carbon-14 in the compounds was demonstrated by oxidation of each compound to benzophenone as described previously.[14] In each case the benzophenone was converted to its 2,4-dinitrophenylhydrazone which was purified by crystallization from dioxane before assaying for carbon-14 content. The radiochemical assay data are given in Table II.

TABLE II

DATA FOR RADIOCHEMICAL STRUCTURE DETERMINATION OF GLYCOLS VIIa AND VIIIc AND THEIR DEAMINATION PRODUCTS, IXa AND IXcd

Compound	Assay mc./mole	Benzophenone 2,4-dinitrophenylhydrazone Assay, mc./mole
VIIIa	2.158	2.131
VIIIc	0.8883	0.9034
IXa	2.158	.0183
IXcd	0.8883	.0826

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(12) C. S. Marvel and W. A. Noyes, THIS JOURNAL, **42**, 2259 (1920).

(13) A. McKenzie and F. Barrow, *J. Chem. Soc.*, **103**, 1331 (1913).

(14) C. J. Collins, THIS JOURNAL, **77**, 5517 (1955).

OAK RIDGE, TENN.

[CONTRIBUTION FROM THE LABORATORIES OF THE PITTSBURGH PLATE GLASS CO. AND THE ALDRICH CHEMICAL CO.]

Unsaturated Phenols. IV.[1] Crotylphenols

BY ALFRED R. BADER[2]

RECEIVED JUNE 20, 1957

Butadiene reacts with phenol in the presence of some Friedel–Crafts catalysts to yield largely a mixture of butenylphenols, with some higher phenols and ethers. *o*- and *p*-crotylphenol have been characterized. A correlation between the acidity functions of acid actalysts and their activity is discussed.

Although the synthesis of compounds related to the tocopherols has prompted studies of the reactions of phenols, specifically hydroquinones, with butadiene,[3] isoprene,[4] 2,3-dimethylbutadiene[4] and phytadiene,[5] the reaction of the simplest phenol with the simplest diene has been described only briefly. A patent[6] has alleged that *p*-crotylphenol is the major component of the monoalkenylphenolic fraction formed in 36% yield in the high temperature reaction of phenol with butadiene catalyzed by solid phosphoric acid.[7] Proell[8] has described the reaction of butadiene with phenol catalyzed by alkanesulfonic acid yielding a mixture of butenylphenols. Claisen[9] had previously described the preparation of chromans from phenol and dienes such as isoprene, and the preparation of pentenylphenols from these reactants under milder conditions has been studied by Pines and Vesely.[10]

The reaction of phenol with 1,3-butadiene at

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(1) For paper III, see THIS JOURNAL, **78**, 1709 (1956).

(2) Aldrich Chemical Co., Milwaukee 12, Wisconsin.

(3) L. I. Smith and J. A. King, THIS JOURNAL, **63**, 1887 (1941).

(4) L. F. Fieser, W. P. Campbell, E. M. Fry and M. D. Gates, *ibid.*, **61**, 3216 (1939).

(5) L. E. Smith, H. E. Ungnade, H. H. Hoehn and S. Wawzonek, *J. Org. Chem.*, **4**, 311 (1939).

(6) R. E. Schaad, U. S. Patent 2,283,465 (May, 1942).

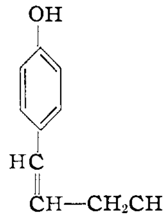
(7) V. N. Ipatieff, U. S. Patents 1,993,512 and 1,993,513 (March, 1935).

(8) W. Proell, *J. Org. Chem.*, **16**, 178 (1951).

(9) L. Claisen, *Ber.*, **54**, 200 (1921); German Patent 374,142 (April, 1923).

(10) H. Pines and J. A. Vesely, U. S. Patents 2,553,470 and 2,578,206 (May and December, 1951). Details of the reaction of phenol with isoprene will be described in paper V of this series.

room temperature in the presence of relatively mild Friedel–Crafts catalysts yields largely butenylphenols accompanied by only small amounts of ethers and higher phenols. Fractionation of the butylphenols obtained on hydrogenation showed the presence of *o*- and *p*-*n*-butylphenols, identified by physical constants and solid derivatives. Thus the possible structures for the original reaction products are *p*-1-butenylphenol (I), *p*-crotylphenol (II), *p*-3-butenylphenol (III) and the three corresponding *o*-substituted isomers. The absence of conjugated isomers such as I was shown by ultraviolet spectra and infrared spectra of the mixed butenylphenols and of cuts obtained by fractional distillation indicated the presence mainly of *o*- and *p*-crotylphenol.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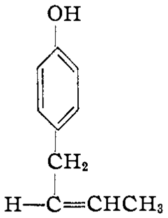
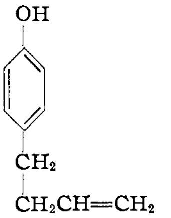

II


III

Low temperature crystallizations of the highest boiling butenylphenol fraction yielded a crystalline solid, m.p. 39°, the infrared spectrum of which shows a strong band at 10.35 μ, indicative of a symmetrically disubstituted *trans* double bond and no bands at 10.1–10.2 and 11.0 μ, characteristic of the vinyl group $RCH{=}CH_2$.[11] The spectrum of this crystalline isomer also shows an intense band at 12.1 and no absorption at 13.3 μ, and this evidence for *p*-substitution is in accord with this isomer's quantitative hydrogenation to the known[12] *p*-*n*-butylphenol. Assignment of structure II to this solid isomer was confirmed by its ultraviolet spectrum and by its isomerization by palladized charcoal to the conjugated isomer I, m.p. 85–86°.[1]

Fractionation of the non-crystallizable mono-butenylphenols boiling over a 20° range and examination of the fractions' infrared spectra showed that the intensities of the band at 12.1 μ increased and those of the band at 13.3 μ decreased with increasing b.p., indicating increasing ratios of *p*-butenylphenols in the higher b.p. fractions. The presence of *o*-crotylphenol in an intermediate fraction was confirmed by the preparation of its phenylurethan melting at 65–66°, identical with the derivative of authentic *o*-crotylphenol.[13]

When titanium tetrachloride, alkanesulfonic acids or the aluminum chloride solvates were the catalysts, the non-crystallizable butenylphenol fractions showed no bands at 10.25 and 10.95 μ, whereas weak bands were present at those wave lengths in the spectra of the butenylphenols obtained with the other catalysts. Theoretically, *n*-butenylphenols with terminal unsaturation as in III are improbable as products of alkenylation,[14] and the weak bands at 10.25 and 10.95 μ may be caused by small amounts of methallyl- or *cis*-crotylphenols.[15]

Butadiene is less reactive than cyclopentadiene, and 85% phosphoric acid, the preferred[14] catalyst for the cycloalkenylation of phenol at 25°, is ineffective with butadiene at that temperature. As has been pointed out by Price,[16] only few direct comparisons of the relative activities of Friedel–Crafts catalysts are recorded in the literature. The composition of the products of the reaction of butadiene with phenol varies greatly with different catalysts, and it seemed of interest to compare the activities of a number of catalysts in this reaction. Comparison is complicated by the involvement of two reactions in the formation of 1:1 adducts, *i.e.*, the alkenylation and the acid-catalyzed ring closure of the *o*-isomer[17] and by further reactions of the alkenylphenols by oxidation and condensation.

Axe[18] has implied that the complex prepared by *saturating* phosphoric acid with boron fluoride, which is an effective catalyst in the butenylation of benzene, also can be used in the alkenylation of phenol. Actually, the use of this as of other strong Friedel–Crafts catalysts such as aluminum chloride and concentrated sulfuric acid leads almost exclusively to ethers and resinous products. The saturated BF_3-phosphoric acid catalyst diluted with an equal weight of 85% phosphoric acid is, however, one of the catalysts of choice; with it or with a mixture of phosphoric and sulfuric acids the mixed butenylphenols are accompanied by only small amounts of ethers and higher phenols. Aqueous sulfuric acid, titanium tetrachloride, alkanesulfonic acids,[8] arenesulfonic acids, aluminum chloride alcoholate and etherate and mixtures of polyphosphoric acid and phosphoric acid also catalyze the mono-butenylation at 15–25°.

The reaction temperature and the catalyst composition direct the orientation. With the complex of phosphoric acid and boron fluoride or with alkanesulfonic acids, *p*-substitution predominates at 15–25°, whereas II constitutes only 30% of the mono-butenylphenols when aqueous sulfuric acid is used at that temperature. This dependence of the product composition on the negative ion associated with the carbonium ion suggests that alkenylations do not involve simply the electrophilic attack on phenol of the diene's free, resonant carbonium ion.

The ranges of composition of the effective cat-

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[11] (a) H. W. Thompson and D. H. Whiffen, *J. Chem. Soc.*, 1412 (1948); (b) N. Sheppard and G. Sutherland, *Proc. Roy. Soc.* (*London*), *A* **196**, 195 (1949); (c) D. Barnard, L. Bateman, A. J. Harding, H. P. Koch, N. Sheppard and G. B. B. M. Sutherland, *J. Chem. Soc.*, 915 (1950).

[12] E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1941, p. 265.

[13] L. Claisen and E. Tietze, *Ber.*, **59B**, 2351 (1926).

[14] A. R. Bader, THIS JOURNAL, **75**, 5967 (1953).

[15] H. Pines, B. Kvetinskas, J. A. Vesely and E. Baclawski, *ibid.*, **73**, 5173 (1951), have claimed on the basis of infrared spectra and hydrogenation to 2-*n*-butylthiophene that the products of the reaction of thiophene with butadiene are 2-(3-butenyl)-thiophene and 2-crotylthiophene. The evidence for the presence of the former was two bands at 910 and 970 cm.$^{-1}$, thought to be indicative of a vinyl group. However, the band at 970 cm.$^{-1}$ (10.3 μ) is at too long a wave length to be indicative of a vinyl group which never absorbs even in allylic substitution products[11c] and in 2-vinylthiophene with a conjugated, possibly perturbed group at more than 10.2 μ. Perhaps the lower boiling butenylthiophene is 2-*cis*-crotylthiophene.

[16] C. C. Price in R. Adams, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 2.

[17] See D. S. Tarbell, *ibid.*, Vol. II, pp. 18, 27.

[18] W. N. Axe, U. S. Patent 2,471,922 (May, 1949).

alyst mixtures are quite narrow, particularly with sulfuric acid (68–70% at 15–25°). Except for aqueous sulfuric acid, the acid catalysts effective for the mono-butenylation at room temperature have acidity functions[19] H_0 of *ca.* −6 to −7, corresponding to 77–83% aqueous sulfuric acid. It may be that but for its oxidizing action, say, 80% aqueous sulfuric acid would be the optimum concentration, and that 68–70% is the highest concentration not causing oxidation of the α-methylene group and the lowest catalyzing the alkenylation.[20] Once one effective catalyst is known in a given reaction, the determination of its acidity function appears helpful in suggesting the most convenient catalyst of similar H_0 to be tried.

Weaker catalysts such as 85% phosphoric acid become effective at higher temperatures; the resulting products contain largely *o*-substituted phenols. The reaction at 200° following the procedure of Schaad[6] yielded only a small amount of mixed mono-butenylphenols from which no *p*-crotylphenol could be isolated. The infrared spectrum of the mixture suggested that it consisted largely of *o*-substituted phenols.

Experimental

Butenylphenols.—To a stirred and cooled mixture of 940 g. (10 moles) of phenol, 1000 cc. of toluene, 100 g. of the complex prepared by saturating[21] 85% phosphoric acid with gaseous boron fluoride and 100 g. of 85% phosphoric acid, there was added slowly a cold solution of 270 g. (5 moles) of butadiene in 1000 cc. of toluene. The reaction was slightly exothermic, and the stirred mixture, which became faintly yellow, was kept at room temperature for 16 hr. It was then diluted with water, the toluene solution was washed and the solvent, unreacted phenol and a small amount of ethers removed by distillation *in vacuo*. The main fraction (659 g., 89%), b.p. 53–90° (0.1 mm.), $n^{25}\text{D}$ 1.539, $\lambda_{\max}^{\mathrm{EtOH-0.1\%\ HOAc}}$ 225 mμ (log ϵ 3.9) and 279 mμ (log ϵ 3.3), mixed butenylphenols, was a colorless oil, completely soluble in aqueous alkali. The yellow flask residue consisted of dibutenylphenols and higher phenols and ethers.

The mixed butenylphenols (180 g.) were fractionated through a 10″ column into 5 fractions: A, 5 g., b.p. 53–55° (0.1 mm.), $n^{25}\text{D}$ 1.5377; B, 25 g., b.p. 55–60° (0.1 mm.), $n^{25}\text{D}$ 1.5380; C, 28 g., b.p. 60–63° (0.1 mm.), $n^{25}\text{D}$ 1.5385; D, 8 g., b.p. 63–69° (0.1 mm.), $n^{25}\text{D}$ 1.5390; and E, 9 g., b.p. 69–72° (0.1 mm.), $n^{25}\text{D}$ 1.5385; their infrared spectra are in accord with those of two-component mixtures, progressing steadily from A (strong band at 13.3 μ, mostly *o*-crotylphenol) to E (strong band at 12.1 μ, mostly *p*-crotylphenol). The colorless flask residue (103 g.) crystallized in the ice-box; two low temperature crystallizations from ligroin yielded 75 g. of soft needles, m.p. 39°, of p-crotylphenol (**II**); $\lambda_{\max}^{\mathrm{EtOH-0.1\%\ HOAc}}$ 225 mμ (log ϵ 3.99), 279 mμ (log ϵ 3.29); $\lambda_{\min}$ 215 mμ (log ϵ 3.84), 247.5 mμ (log ϵ 2.10).

Anal.[22] Calcd. for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found, mixed mono-phenols: C, 81.06; H, 8.04. Found, fraction C: C, 80.82; H, 8.25. Found, II: C, 81.22, 81.07; H, 8.37, 8.19.

The solid isomer, II, was characterized by a *p*-**nitrophenylurethan** which formed white needles from aqueous methanol, m.p. 139–140°, and by a **phenoxyacetic acid** which after two crystallizations from water melted sharply at 80°.

Anal. Calcd. for $C_{17}H_{16}O_4N_2$: C, 65.37; H, 5.16. Found: C, 65.30; H, 5.50. Calcd. for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.85; H, 6.90.

The exothermic reaction of the mixed sodium butenylphenoxides with chloroacetic acid yields a mixture of aryloxyacetic acids, of which one is easily separated through its insolubility in ligroin. Ultraviolet and infrared spectra suggested this to be *o*-**crotylphenoxyacetic acid** which crystallized from water in soft, white needles, m.p. 137°; $\lambda_{\max}^{\mathrm{EtOH-0.1\%\ HOAc}}$ 215.0 mμ (log ϵ 3.94), 271.5 mμ (log ϵ 3.24), 277.5 mμ (log ϵ 3.20); $\lambda_{\min}$ 242.5 mμ (log ϵ 2.28), 275 mμ (log ϵ 3.17). Its infrared spectrum in Nujol mull showed a strong band at 10.3 μ, probably indicative of a *trans* double bond, RCH=CHR′.

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.45; H, 7.04.

Reaction of fraction B with phenyl isocyanate gave a good yield of a crystalline phenylurethan which crystallized in fine needles from methanol, m.p. 65–66°, identical with *o*-crotylphenyl phenylcarbamate.[13]

Anal. Calcd. for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41. Found: C, 76.18; H, 6.19.

Hydrogenation of II (methanol, Adams platinum oxide catalyst, 100°) quantitatively yielded *p*-*n*-**butylphenol**,[12] m.p. 20–21°, $n^{25}\text{D}$ 1.5176, characterized by a phenoxyacetic acid, m.p. 80–81°.

Hydrogenation of the mixed butenylphenols (50 g.) yielded mixed *n*-butylphenols (50 g.), $n^{25}\text{D}$ 1.517, which fractional distillation separated into 15 g. of *o*-*n*-butylphenol, b.p. 94–97° (8 mm.), $n^{25}\text{D}$ 1.518, characterized by a crystalline phenoxyacetic acid[23] (crystallized from ligroin), m.p. 104–105°; and 24 g. of *p*-*n*-butylphenol, b.p. 113–116° (8 mm.), $n^{25}\text{D}$ 1.518, characterized as above.

A small quantity of ethers (3–6%) is formed in this room temperature reaction; these distil with unreacted phenol and can be separated by their insolubility in alkali. Their boiling range (205–225°) and the physical constants of the higher b.p. fraction (b.p. 220–225°, $n^{25}\text{D}$ 1.530, d^{25}_{25} 1.020) suggest that these ethers are a mixture of 2-ethylcoumaran and 2-methylchroman.[24]

The second catalyst of choice is a mixture of 85% phosphoric acid and concd. sulfuric acid. Adding a cooled solution of butadiene (60 g., 1.1 moles) in toluene (100 cc.) to a stirred mixture of phenol (94 g., 1 mole), toluene (100 cc.), 85% phosphoric acid (100 g.) and sulfuric acid (sp. gr. 1.84, 15 g.) and keeping the stirred mixture at 15–25° for 16 hr. yielded 115 g. (0.78 mole, 78%) of mixed butenylphenols a colorless oil, b.p. 80–120° (1.5 mm.), $n^{25}\text{D}$ 1.5385. The infrared spectrum of this mixture was similar to that of the mixed butenylphenols prepared with boron fluoride and phosphoric acid, and crystalline II was isolated from the higher b.p. fraction.

With 68% aqueous sulfuric acid and equimolar amounts of phenol and butadiene at 15°, the yield of mono-butenylphenols is 70%. Fractional distillation showed these to consist of *ca.* 60% *o*-crotylphenol and 30% of the crystalline isomer II.

The reactions catalyzed by boron fluoride, by the complex of phosphoric acid saturated with boron fluoride, by concd. sulfuric acid and by aluminum chloride are very exothermic and lead largely to higher phenols and ethers. Fair yields of butenylphenols are obtainable with polyphosphoric acid or, preferably, with mixtures of polyphosphoric acid and 85% phosphoric acid (2:1), titanium tetrachloride arenesulfonic acids and the aluminum chloride–alcohol and –ether complexes. Again, crystalline II was isolated by low temperature crystallizations from heptane from all mixed butenylphenols. Also, the higher b.p. liquid butenylphenol prepared by the procedure of Proell[8] crystallized at once on cooling and proved identical with II.

Zinc chloride and 85% phosphoric acid are inactive at 10–40°. Phosphoric acid (85%) becomes effective at 100–125°; at 140° the bulk of the product consists of ethers and higher phenols. Comparison of spectra showed that the maximum at 13.3 μ was more than that at 12.1 μ somewhat less intense than the corresponding maxima in the infrared spectra of mixed mono-butenylphenols prepared at lower temperatures, indicating somewhat more *p*-substitution in the latter.

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[19] L. P. Hammett and A. J. Deyrup, THIS JOURNAL, **54**, 2721 (1932); L. P. Hammett and M. A. Paul, *ibid.*, **56**, 827 (1934). I am much indebted to Mr. John E. Hyre for the determination of the acidity functions of the catalysts.

[20] I wish to thank Professor Paul D. Bartlett for this suggestion.

[21] 85% sirupy phosphoric acid exothermically absorbs approx. its weight of boron fluoride.

[22] Analyses by the Micro-Tech Laboratories, Skokie, Ill.

[23] G. Sandulescu and A. Girard, *Bull. soc. chim.*, [4] **47**, 1300 (1930).

[24] C. D. Hurd and W. A. Hoffman, *J. Org. Chem.*, **5**, 212 (1940); W. Baker and J. Walker, *J. Chem. Soc.*, 646 (1935).

From the product of the reaction described by Schaad[6] (77 g. of phenol, 20 g. of butadiene, 25 g. of U.O.P. polymerization catalyst #2, 200°, 4 hr.), there was obtained besides much unreacted phenol, 11 g. of a phenolic fraction, A, b.p. 65–130° (1 mm.), $n^{25}D$ 1.540; and 30 g. of dark, resinous material. The spectrum of A showed a strong band at 13.3 μ characteristic of *o*-substitution, only a weak band at 12.1 μ and no band at 10.35–10.40 μ, the position of one of the strongest bands of II, indicative of a symmetrically disubstituted *trans* double bond.

Acidity Functions.[19]—With anthraquinone as the Hammett indicator, the alkanesulfonic acid and polyphosphoric acid and the mixtures of 85% phosphoric acid and sulfuric acid and of polyphosphoric acid and phosphoric acid used as catalysts at 15–25° show acidity functions H_0 ranging from -6 to -7. The H_0 of 68–70% aqueous sulfuric acid is -5.0 to -5.2.

***p*-1-Butenylphenol (I).**—A mixture of 90 g. of II and 5 g. of 5% palladium-on-charcoal (Baker and Co., lot #785, activity 985) was refluxed under inert gas for 25 minutes when the reaction temperature had risen to 260°. The product was dissolved in ligroin and filtered, the solvent removed and the red, viscous oil (86 g.) distilled to yield a first fraction A (46 g.), b.p. 80–150° (0.5 mm.); a second fraction B (19 g.), b.p. 150–210° (0.5 mm.); and an orange resinous residue (18 g.). Crystallization of A from heptane yielded 5.5 g. of shiny, white platelets of the less soluble isomer I, identical with the compound prepared by alkali isomerization[1] of II. The infrared spectra of I and II in carbon disulfide are quite similar, except that I exhibits an intense band at 11.8 μ absent in the spectrum of II. The heptane mother liquor from I yielded 40 g. of unreacted II. Fraction B consisted largely of a colorless dimeric diphenol, b.p. 187–190° (0.4 mm.), which was accompanied by a fiery red impurity.

Anal. Calcd. $C_{20}H_{24}O_2$: C, 81.04; H, 8.16. Found: C, 80.79; H, 8.13.

Butenylanisoles.—Anisole reacts much like phenol at 10–30°; mixed butenylanisoles were prepared in good yields with concd. sulfuric acid and with a 2:1 mixture of polyphosphoric acid and 85% phosphoric acid; b.p. 75–110° (10 mm.), $n^{25}D$ 1.519, strong bands at 12.1 and 13.3 μ, indicating *o*- and *p*-substitution.

Anal. Calcd. for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.87; H, 9.00.

Acknowledgment.—I wish to thank Professors M. G. Ettlinger and C. D. Hurd for valuable advice.

MILWAUKEE, WISCONSIN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

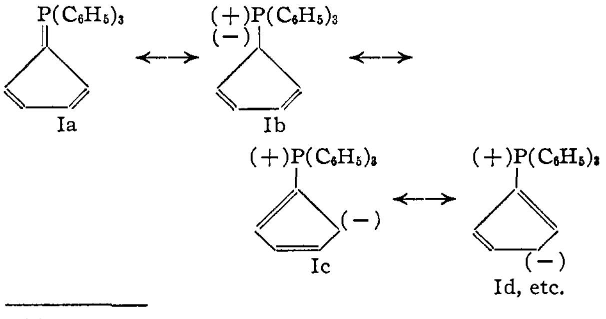
Phosphinemethylenes. III. A New Class of Azo Dyes Containing Phosphorus

BY FAUSTO RAMIREZ AND STEPHEN LEVY[1]

RECEIVED MAY 22, 1957

Triphenylphosphoniumcyclopentadienylide (I) couples readily with diazonium salts producing a new class of brightly colored azo dyes. The coupling reaction occurs at a position in the five-membered ring which preserves the stable cyclopentadienide system and which gives rise to the longest of the possible conjugated systems terminating at a phosphorus atom. The ultraviolet and infrared absorption spectra, and the dipole moment are described for the coupling products (VI and VII) from benzenediazonium chloride and *p*-nitrobenzenediazonium chloride. With hydrobromic acid, the azophosphinemethylenes VI and VII yield phenylhydrazones of a simple phosphonium derivative of cyclopentadienone (VIII and IX). The reaction of triphenylphosphine with pure *cis*-3,5-dibromocyclopentene leads, after alkaline treatment, to triphenylphosphoniumcyclopentadienylide (I) in yields comparable to those realized when the phosphine is added to the mixture of dibromides resulting from cyclopentadiene and bromine in chloroform solution.

Recent investigations in this Laboratory[2] have led to the preparation of several new types of phosphinemethylenes or phosphorus ylides[3] ($R_3P{=}CXY \longleftrightarrow R_3\overset{(+)}{P}{-}\overset{(-)}{C}XY$), and to the examination of their physical and chemical properties. Of particular interest is triphenylphosphoniumcyclopentadienylide[2a] (I), a remarkably stable, pale yellow, high melting (229–231°) substance with a dipole moment (6.99 D) which suggests roughly equal contributions from a homopolar structure, presumably Ia, and several dipolar forms (Ib-Id).



Ia Ib Ic Id, etc.

In line with recent views on non-benzenoid aromatic systems,[2a] it appeared of interest to explore the behavior of the phosphinemethylene I toward electrophilic reagents. This paper is concerned with the coupling reaction of I and diazonium salts.

The Reaction of Triphenylphosphoniumcyclopentadienylide (I) with Diazonium Salts. Coupling Reaction with Benzenediazonium Chloride (II).—The course of this reaction and the proof of structure of the product are formulated in Chart I. When a methylene chloride solution of the phosphinemethylene I was added to an aqueous solution of benzenediazonium chloride (II), buffered with sodium acetate, an immediate reaction occurred. The reddish-orange substance, m.p. 239–240°, which was isolated in 88% yield, had the formula $C_{29}H_{23}N_2P$ and was shown to be triphenylphosphonium-(2-phenylazo)-cyclopentadienylide (VI). This structure was established as follows. (1) The coupling product or azophosphinemethylene VI was converted by hydrobromic acid into an orange **hydrobromide** VIII of m.p. 236–237° and formula $C_{29}H_{24}N_2PBr$. (2) This hydrobromide VIII had the structure of a cyclopentadienone-phenylhydra-

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[1] Texas Co. Fellow, 1956–1957. From part of the Ph.D. Thesis of S. Levy.

[2] (a) F. Ramirez and S. Levy, THIS JOURNAL, **79**, 67 (1957); (b) F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 41 (1957); (c) THIS JOURNAL, **78**, 5614 (1956).

[3] For the nomenclature of these compounds, see ref. 2b, footnote 1. References to past and current work on phosphinemethylenes are found in ref. 2 and in G. Wittig, *Experientia*, **12**, 41 (1956).