

***cis*-1-Methyl-2-carboxycyclohexaneacetic Acid (XVI).**—A 0.056-g. sample of sublimed unsaturated acid XV, m.p. 197–198°, was dissolved in 18 ml. of purified (by refluxing over Raney nickel) 0.1% sodium hydroxide solution, and hydrogenated at room temperature and atmospheric pressure over 0.05 g. of 10% palladium-on-carbon (American Platinum Works) which had already been suspended in 10 ml. of water and equilibrated over hydrogen. After 20 hours of stirring the calculated amount of gas had been absorbed and no further reaction was occurring. The mixture was filtered and the filtrate and washings were concentrated to about 50 ml. Acidification with concentrated hydrochloric acid gave 0.0125 g. of colorless crystals, m.p. 160–167°. Concentration of the mother liquors gave a second crop of 0.0075 g., m.p. 160–167°, and further concentration gave two additional crops amounting to 0.027 g., m.p. 120–127°, possibly containing considerable of the *trans* isomer (see below). The first two crops were combined and recrystallized twice from water, m.p. 172–173.5°. Further recrystallization did not raise the m.p. There was

no depression of the m.p. on admixture with an authentic specimen of the *cis* acid XVI, m.p. 171.5–172.5° (reported<sup>9</sup> 171.5–172°) prepared by the method of Linstead and Millidge.<sup>9</sup> The infrared spectra of the two samples determined in Nujol mull were identical.

***trans*-1-Methyl-2-carboxycyclohexaneacetic Acid.**—A 0.02-g. sample of the *cis* isomer produced in the hydrogenation experiment described above was epimerized by heating with 10 ml. of concentrated hydrochloric acid for 16 hours at 200° according to the procedure of Linstead and Millidge.<sup>9</sup>

After two recrystallizations from water it melted at 133–134°. Further recrystallization did not change the m.p. There was no depression of the m.p. on admixture with authentic *trans* acid, m.p. 131.5–132.5° (reported<sup>9</sup> 131–132°) obtained by isomerization of the authentic *cis* acid mentioned above. The infrared spectra of the two specimens of the *trans* acid determined in Nujol mull were identical except for slight irregularities which may be attributed to differences in impurities.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE PAINT DIVISION OF THE PITTSBURGH PLATE GLASS COMPANY]

## Cyclopentenylphenols

BY ALFRED R. BADER

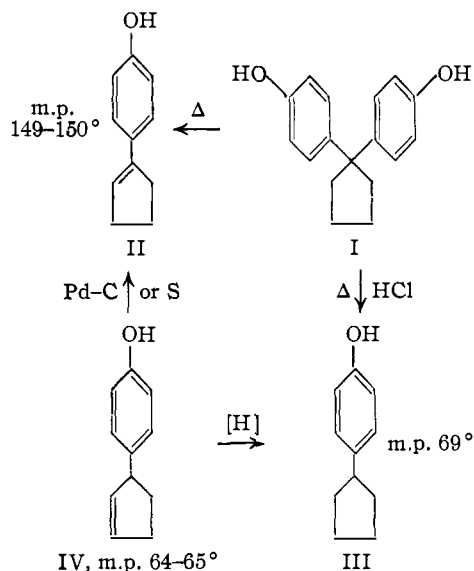
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The reaction of phenol with cyclopentadiene at 25° in the presence of phosphoric acid yields mainly *p*-2-cyclopentenylphenol IV, while *o*-2-cyclopentenylphenol VII is the major phenolic product at higher temperatures.

Cyclopentyl- and cyclopentenylphenols have hitherto been accessible only *via* cyclopentenyl chloride,<sup>1</sup> the Friedel-Crafts alkylation of phenol<sup>2</sup> and anisole<sup>3</sup> with cyclopentanol and cyclopentanone, and the decomposition of *p*-cyclopentylidenediphenol (I).<sup>4</sup>

The only recorded attempt to alkylate phenol with cyclopentadiene appears to have been that of v. Braun and Kühn<sup>1</sup> who obtained viscous oils in the reaction catalyzed by hydrochloric acid.

The availability of cyclopentadiene and the hope of preparing unsaturated, non-conjugated phenols for isomerization studies prompted the reinvestigation of its reactions with phenol. At room temperature and with substantial quantities of phosphoric acid, *p*-2-cyclopentenylphenol IV is formed in *ca.* 70% yield. This is a crystalline solid, m.p. 64–65°, characterized by a *p*-nitrophenylurethan, m.p. 174°. The phenol IV can be isomerized by palladium-on-charcoal or by sulfur to the known<sup>4</sup> *p*-1-



(1) J. v. Braun and M. Kühn, *Ber.*, **60**, 2551 (1927). Professor Martin G. Ettlinger has kindly pointed out that v. Braun and Kühn's *o*-2-cyclopentenylphenol probably was the product of C-alkylation rather than of Claisen rearrangement of phenyl cyclopentenyl ether as these authors believed. The ether, which these authors never had in hand, could not undergo normal rearrangement with inversion, for the transition state would be sterically improbable and would virtually violate Bredt's rule. The analogous 2-cyclohexenyl phenyl ether (J. W. Cornforth, G. K. Hughes and F. Lions, *J. Proc. Royal Soc. N. S. Wales*, **71**, 323 (1938); *C. A.*, **33**, 148 (1939), yields as the major products, phenol and cyclohexadiene. Furthermore, the cyclopentenyl ether of *o*-2-cyclopentenylphenol which v. Braun and Kühn apparently did have gave no 2,6-dicyclopentenylphenol on distillation, but cleaved to cyclopentadiene and *o*-2-cyclopentenylphenol. A direct C-alkenylation under conditions similar to those of v. Braun and Kühn is described by L. Claisen and E. Tietze, *Ber.*, **59**, 2344 (1926).

(2) German Patent 615,448.

(3) C. Mentzer, D. Molho and D. Xuong, *Bull. soc. chim.*, 263 (1948).

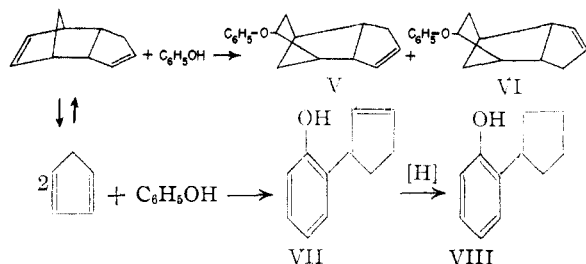
(4) J. v. Braun, E. Anton, W. Haensel and G. Werner, *Ann.*, **472**, 1 (1929).

cyclopentenylphenol (II), melting at 149–150°, and hydrogenation of IV yields *p*-cyclopentenylphenol (III), which had been reported to melt at 56°<sup>2</sup> and at 63–65°<sup>4</sup> and which, when pure, melts at 69°.

When dicyclopentadiene and phenol are refluxed with a catalytic amount of phosphoric acid, the dimer reacts in part to yield the known<sup>5</sup> solid phenoxydihydro-exo-dicyclopentadiene, V or VI, and a liquid isomer thereof, and in part decomposes to cyclopentadiene which then alkylates phenol in the ortho position. The identity of the crystalline ether with that prepared by Bruson and Riener by the sulfuric acid-catalyzed reaction of dicyclopentadiene with phenol at 30° was established by direct comparison, and by the preparation of identical di-

(5) H. A. Bruson and T. W. Riener, *THIS JOURNAL*, **68**, 8 (1946).

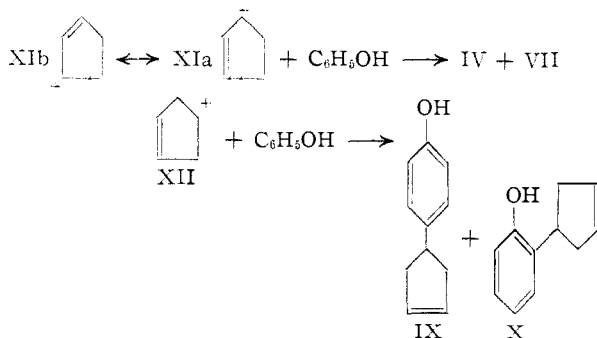
hydro and dihydro dibromo derivatives from both. In the high temperature reaction this solid ether is accompanied by about an equal quantity of a liquid isomer having similar infrared and ultraviolet spectra, perhaps of alternate structure V or VI.



The known<sup>1</sup> *o*-2-cyclopentenylphenol (VII) which is the main phenolic product in the high temperature reaction, is a colorless oil, m.p. 3–5°, characterized by a *p*-nitrophenylurethan, m.p. 164°. That little or none of IV is formed under these conditions is indicated by the ease of purification of the derivative and by the quantitative hydrogenation of VII to *o*-cyclopentylphenol (VIII), m.p. 40°, characterized by a *p*-nitrophenylurethan melting at 155–156°.

The ultraviolet spectra of the phenols prepared at 25° and at 150–170° show the absence of conjugated isomers. The phenols IV and VII, like allyl phenol,<sup>6</sup> show two maxima of moderate intensity at *ca.* 225 and 275 m $\mu$ , while the higher intensity maximum of conjugated phenols such as II and propenylphenol<sup>7</sup> is shifted to *ca.* 260 m $\mu$ .

A consideration of the mechanism of formation of these cyclopentenylphenols suggests structures IX and X rather than the alternate structures IX and X. Addition of a proton to cyclopentadiene can lead to the resonant carbonium ion XIa  $\longleftrightarrow$  XIb and thence to IV and VII; the alternate carbonium ion XII is not stabilized by resonance.



There was no evidence of a third *para*-substituted isomer in the high temperature palladium-on-charcoal catalyzed isomerization of IV, and this indirectly confirms the structure assigned.

Recently Pines and Vesely<sup>8</sup> have investigated the reactions of dienes, specifically isoprene, with phenol, and have concluded that "if both double bonds of the diene are tertiary or non-tertiary, each pos-

esses the same order of reactivity, and it is difficult to react one double bond and not the other." The work here reported, and the reactions of butadiene with phenol,<sup>9</sup> trimethylhydroquinone,<sup>10</sup> and thiophene<sup>11</sup> suggest that such a generalization can apply only to the specific catalyst systems studied.

## Experimental

*p*-2-Cyclopentenylphenol (IV).—To a stirred mixture of 940 g. (10 moles) of phenol in 1000 cc. of toluene and 300 g. of 85% sirupy phosphoric acid at 25°, there was added slowly a cooled solution of 330 g. (5 moles) of freshly distilled cyclopentadiene in 500 cc. of toluene. The reaction was slightly exothermic. The mixture became deep purple and was cooled and stirred at room temperature for 18 hours. Anhydrous sodium carbonate (180 g.) was then added, the mixture was filtered and the red filtrate was fractionated. After removal of solvent, some water, dicyclopentadiene, and phenol, there was obtained a colorless oil (45 g.), b.p. 80–110° (1.2 mm.), largely *o*-2-cyclopentenylphenol, and a main fraction (480 g., 67%) b.p. 110–135° (1.2 mm.), of *p*-2-cyclopentenylphenol which crystallized in the receiver, and after two low temperature crystallizations from ligroin formed white needles, m.p. 64–65°, b.p. 114–117° at 1.5 mm.

In this preparation, the amount of catalyst, the reaction temperature, the solvent and the amount of diene added can be varied appreciably without materially affecting the yield. However, with small amounts of catalyst, or with larger quantities of cyclopentadiene, more higher phenols are formed. Slight cooling is sufficient to keep the reaction temperature below 40°; if the temperature is kept below 25°, the mixture does not become purple but the improvement in yield is insignificant. Mixtures of ligroin and benzene or toluene can serve as solvent; with ligroin alone the phenol-phosphoric acid complex becomes very viscous.

The product of m.p. 64–65° possessed these properties:  $\lambda_{\text{max}}^{\text{EtOH-0.1\% HOAc}}$  225 m $\mu$  (log *e* 3.99); 279 m $\mu$  (log *e* 3.30).

The infrared spectrum in CS<sub>2</sub> showed a hydroxyl band at 2.82  $\mu$  and a strong band at 12.11  $\mu$ , indicative of *para*-substitution.

*Anal.* Calcd. for C<sub>11</sub>H<sub>10</sub>O: C, 82.46; H, 7.55. Found: C, 82.20, 82.42; H, 7.62, 7.76.

The phenol IV was characterized by a *p*-nitrophenylurethan which formed brittle, white needles from aqueous methanol, melting at 174–175° and strongly depressing the m.p. of the *p*-nitrophenylurethan of *o*-2-cyclopentenylphenol, but not that of the corresponding derivative of *p*-cyclopentenylphenol.

*Anal.* Calcd. for C<sub>18</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>: C, 66.65; H, 4.97; N, 8.64. Found: C, 67.15; H, 5.20; N, 8.85.

*o*-2-Cyclopentenyl-*p*-cresol.—The similar reaction of *p*-cresol, cyclopentadiene and phosphoric acid in toluene at 25–50° yields a viscous oil with a pleasant, earthy odor, b.p. 105–108° (1.3 mm.), *n*<sub>D</sub><sup>25</sup> 1.5595, *d*<sub>4</sub><sup>25</sup> 1.0570, *M*<sub>R</sub> (calcd.) 52.87, *M*<sub>R</sub> (found) 53.24.  $\lambda_{\text{max}}^{\text{EtOH-0.1\% HOAc}}$  221.0 m $\mu$  (log *e* 3.82); 281.0 m $\mu$  (log *e* 3.39);  $\lambda_{\text{min}}^{\text{EtOH 0.1\% HOAc}}$  217.5 m $\mu$  (log *e* 3.81); 247.5 m $\mu$  (log *e* 2.16).

*Anal.* Calcd. for C<sub>12</sub>H<sub>14</sub>O: C, 82.72; H, 8.10. Found: C, 82.76; H, 8.03.

Isomerization of IV.—Sixty-three grams of IV was distilled from 2 g. of 5% palladium on charcoal.<sup>12</sup> The flask residue (18 g.) was a viscous, dark resin. The distillate (46.5 g.) was separated by solubility in ligroin into the less soluble *p*-1-cyclopentenylphenol (II) (5 g.), and unreacted starting material (36 g.), melting at 55–58° and not depressing the m.p. of pure IV.

The conjugated phenol II forms shiny platelets from aqueous ethanol, m.p. 149–150°.  $\lambda_{\text{max}}^{\text{EtOH-0.1\% HOAc}}$  262.5 m $\mu$  (log *e* 4.27); 290.0 m $\mu$  (inflection, log *e* 3.43);  $\lambda_{\text{min}}^{\text{EtOH-0.1\% HOAc}}$  227.5 m $\mu$  (log *e* 3.36).

The infrared spectrum in CS<sub>2</sub> showed a hydroxyl band at

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

(10) L. I. Smith and J. A. King, *This Journal*, **63**, 1887 (1944).

(6) T. J. Webb, L. I. Smith, W. A. Bastedo, Jr., H. E. Ungnade, W. W. Prichard, H. H. Hoehn, S. Wawzonek, J. W. Opie and F. L. Austin, *J. Org. Chem.*, **4**, 389 (1939).

(7) E. A. Braude, *J. Chem. Soc.*, 1902 (1949); M. Grumez, *Ann. chim.*, **10**, 378 (1938).

(8) H. Pines and J. A. Vesely, U. S. Patents 2,553,470 and 2,578,206 (May and December, 1951).

(11) H. Pines, B. Kvetinskas, J. A. Vesely and E. Baclawski, *ibid.*, **73**, 5173 (1951).

(12) Baker and Co., lot #785, activity 985.

2.79  $\mu$  and strong bands at 12.03 and 12.50  $\mu$ , indicative of para-substitution.

The acetate<sup>4</sup> of II, crystallized from aqueous ethanol, melts at 74°.

The phenol IV can be similarly conjugated by distillation from sulfur. No hydrogen sulfide and more resinous material is formed in this reaction. Surprisingly, IV could not be isomerized by alkali. Studies of the isomerization of this and other unsaturated phenols will be reported in a later paper.

Hydrogenation of IV in methanol with Adams platinum catalyst at 90° quantitatively yielded *p*-cyclopentylphenol (III), which formed soft needles from ligroin melting sharply at 69° and not depressing the m.p. of IV.

*Anal.* Calcd. for C<sub>11</sub>H<sub>14</sub>O: C, 81.44; H, 8.70. Found: C, 81.27; H, 9.06.

The saturated phenol III was characterized by a *p*-nitrophenylurethan which crystallized from methanol in fine needles, m.p. 198–199°.

*Anal.* Calcd. for C<sub>18</sub>H<sub>18</sub>N<sub>2</sub>O<sub>4</sub>: C, 66.24; H, 5.56. Found: C, 66.09; H, 5.45.

**Reaction of Dicyclopentadiene with Phenol.**—A mixture of phenol (2256 g., 24 moles), dicyclopentadiene (660 g., 2.5 moles) and 85% sirupy phosphoric acid (5 g.) was refluxed under inert gas for 22 hours. Unreacted dicyclopentadiene and phenol (1700 g.) were then removed by distillation *in vacuo* and the dark residue (1130 g.) was washed, dried and distilled. The light yellow distillate (895 g.), b.p. 75–190° (0.4 mm.), was separated by solubility in 10% aqueous potassium hydroxide into 330 g. of a phenolic fraction A, and 560 g. of a fraction B, consisting of ethers and cryptophenols.

Fractionation of A yielded as main fraction a colorless oil (260 g.) *o*-2-cyclopentenylphenol (VII), which crystallized in the ice-box, m.p. 3–5°, b.p. 89–91° (0.7 mm.),  $n_D^{25}$  1.5652;  $n_D^{20}$  1.5666;  $d_4^{25}$  1.0755;  $M_R$  (calcd.) 48.26;  $M_R$  (found) 48.50.

The infrared spectrum in CS<sub>2</sub> showed hydroxyl bands at 2.83 and 2.90  $\mu$ , and a strong band at 13.3  $\mu$  indicative of ortho-substitution. This band is absent in the spectrum of IV.  $\lambda_{\max}^{EtOH}$  220 m $\mu$  (log *e* 3.84); 275 m $\mu$  (log *e* 3.38).

*Anal.* Calcd. for C<sub>11</sub>H<sub>12</sub>O: C, 82.46; H, 7.56. Found: C, 81.87; H, 7.55.

Its *p*-nitrophenylurethan forms needles from methanol, m.p. 164°.

*Anal.* Calcd. for C<sub>18</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>: C, 66.65; H, 4.97; N, 8.64. Found: C, 66.87; H, 5.33; N, 8.76.

The next fraction was a colorless oil, b.p. 140–145° (0.5 mm.), largely 2,4-di-(2-cyclopentenyl)-phenol,  $n_D^{25}$  1.5795.  $\lambda_{\max}^{EtOH}$  222 m $\mu$  (log *e* 3.8); 278 m $\mu$  (log *e* 3.4).

*Anal.* Calcd. for C<sub>16</sub>H<sub>18</sub>O: C, 84.91; H, 8.02. Found: C, 84.70, 84.85; H, 7.93, 8.13.

Fractionation of alkali-insoluble B yielded a first fraction (20 g.) of the coumaran XIII, b.p. 85–89° (1.5 mm.),  $n_D^{25}$  1.5535, unchanged by prolonged refluxing at 242°<sup>13</sup>;  $\lambda_{\max}^{EtOH}$  220 m $\mu$  (log *e* 3.67); 282.5 m $\mu$  (log *e* 3.44); 289 m $\mu$  (log *e* 3.33).<sup>14</sup>

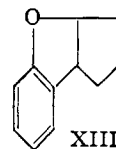
*Anal.* Calcd. for C<sub>11</sub>H<sub>12</sub>O: C, 82.46; H, 7.55. Found: C, 82.65; H, 7.95.

When a mixture of 20 g. of VII, 80 cc. of glacial acetic

(13) Phenyl cyclopentenyl ether would decompose to phenol and cyclopentadiene under these conditions.

(14) The higher wave length maximum of 2-methylcoumaran is similarly resolved. Cf. ref. 6.

acid and 40 cc. of 48% hydrobromic acid was refluxed for 30 minutes, the coumaran XIII was obtained in 70% yield.



The exothermic reaction of bromine with XIII in carbon tetrachloride is accompanied by the evolution of hydrogen bromide. The product, 5(or 7)-bromo-2,3-cyclopentano-2,3-dihydrobenzofuran is an oil, b.p. 124–127° (0.7 mm.),  $n_D^{25}$  1.594.

*Anal.* Calcd. for C<sub>11</sub>H<sub>11</sub>BrO: C, 55.25; H, 4.64. Found: C, 55.02; H, 4.87.

The second fraction (455 g.), a colorless oil, b.p. 145–150° (1.5 mm.),  $n_D^{25}$  1.5624, was separated by solubility in methanol into approximately equal parts of a more soluble, colorless oil,  $n_D^{25}$  1.564, and a crystalline solid which formed white needles from methanol, m.p. 69–70°. Their ultraviolet and infrared spectra were indistinguishable. The m.p. of the solid isomer was not depressed by admixture with an authentic sample of the solid phenoxydihydro-exo-dicyclopentadiene,<sup>5</sup>  $\lambda_{\max}^{EtOH}$  222.5 m $\mu$  (log *e* ca. 3.8<sup>15</sup>); 273 m $\mu$  (log *e* 3.25), 279 m $\mu$  (log *e* 3.18).

*Anal.* Calcd. for C<sub>16</sub>H<sub>18</sub>O: C, 84.91; H, 8.02. Found: (solid isomer): C, 84.57; H, 8.11. (liquid isomer): C, 84.54; H, 8.13.

Hydrogenation of the solid isomer and of the ether prepared after Bruson and Riener<sup>6</sup> (methanol, Adams platinum catalyst, 100°) yielded identical colorless oils, m.p. 23–25°, the phenoxytetrahydro-exo-dicyclopentadiene.

*Anal.* Calcd. for C<sub>16</sub>H<sub>18</sub>O: C, 84.16; H, 8.83. Found: C, 84.77; H, 9.03.

Bromination of both in glacial acetic acid yielded identical samples of the 2,4-dibromophenoxytetrahydro-exo-dicyclopentadiene which forms white shiny needles from methanol, m.p. 68–69°.

*Anal.* Calcd. for C<sub>18</sub>H<sub>18</sub>Br<sub>2</sub>: C, 49.76; H, 4.70. Found: C, 49.70; H, 4.89.

The third fraction (37 g.), a colorless oil, b.p. 155–160° (0.8 mm.),  $n_D^{25}$  1.5790, is probably a mixture of higher ethers and cryptophenols, as its infrared spectrum shows a strong hydroxyl band at 2.83  $\mu$ .

Hydrogenation of VII in methanol with Adams catalyst at 100° quantitatively yielded *o*-cyclopentylphenol (VIII), which formed white needles from ligroin, m.p. 40°.<sup>16</sup>

*Anal.* Calcd. for C<sub>11</sub>H<sub>14</sub>O: C, 81.44; H, 8.70. Found: C, 81.69; H, 8.95.

Its *p*-nitrophenylurethan formed white needles from methanol, m.p. 155–156°.

*Anal.* Calcd. for C<sub>18</sub>H<sub>18</sub>N<sub>2</sub>O<sub>4</sub>: C, 66.24; H, 5.56. Found: C, 66.53; H, 5.42.

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(15) The intensity of this band changes quite rapidly; the spectrum above 255 m $\mu$  is not affected.

(16) Reference 2 gives its m.p. as 34–35°.