

(R = H); II (R = CH₃); III (R = *t*-C₄H₉);
IV (R = Cl)

I with a diene was that of Nara Boon-Long,³ who reported the formation of ill-characterized and possibly polymeric products when a solution of I in benzene was heated with 2,3-dimethyl-1,3-butadiene in a sealed tube at 100° for 24 hours. The rather vigorous conditions and lack of control experiments prompted us to reinvestigate the reaction.

The first of our difficulties was encountered in the preparation of the parent compound, I. It had first been synthesized by Willstätter and Kalb⁴ who oxidized an ether solution of 4,4'-diphenol by shaking with a suspension of lead dioxide at room temperature for 24 hours. Subsequent workers^{5,6} also employed this procedure⁷ but noted that the method was inconsistent, and did not always result in the desired product. In our hands, using commercially manufactured lead dioxide, the method was a complete failure. The state of subdivision or the recrystallization solvent for the 4,4'-diphenol, factors which were claimed to be of importance,⁵ had little effect. It was found, however, that if the lead dioxide was freshly prepared from lead tetraacetate in a highly active form, according to the recent procedure of Kuhn and Hammer,⁸ and the reaction time for the oxidation was decreased from 24 hours to about 30 minutes or less, a reasonable yield (55%) of the red crystalline modification of I was consistently obtained.

No exothermic reaction occurred between I and cyclopentadiene in alcohol, benzene, or chloroform solvents, nor could any well-defined adduct be obtained by refluxing. Blank experiments showed that I is readily polymerized by refluxing in the above solvents, but that II can be recovered quantitatively, even when cyclopentadiene is present.

The absorption spectra of I and of several sub-

TABLE I
MAXIMA IN THE VISIBLE AND ULTRAVIOLET ABSORPTION
SPECTRA OF SOME DIPHENOQUINONES

Com- pound	λ^c	ϵ	λ	ϵ	λ	ϵ	λ	ϵ
I ^a	395	62,600	261	2990	252	3130
II ^a	414	67,600
III ^a	420	70,800	269	4920	260	5480	251	4740
II ^b	421	73,200
III ^b	427	66,000	271	4240	262	4800	253	4320
IV ^b	435	71,800	283	3470	273	4520	261	5390

^a In ethyl alcohol. ^b In chloroform. ^c All wave lengths are in μ .

(3) N. Boon-Long, *J. Pharm. Assoc. Siam*, **1**, 5 (1948); *C. A.*, **43**, 5017 (1949).

(4) R. Willstätter and L. Kalb, *Ber.*, **38**, 1232 (1905).

(5) N. A. Valyashko and M. M. Shcherbak, *J. Gen. Chem. (U.S.S.R.)*, **8**, 1597 (1938); *C. A.*, **33**, 4589 (1939).

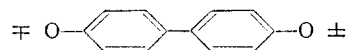
(6) L. F. Fieser, *THIS JOURNAL*, **52**, 4915 (1930).

(7) After developing the successful procedure described below, we noted that L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 2nd Ed., 1941, p. 439, mentions the use of lead tetraacetate to oxidize diphenol to I. We could not find the details of this procedure in the literature, and after four unsuccessful attempts, gave this method up.

(8) R. Kuhn and I. Hammer, *Ber.*, **83**, 413 (1950).

stituted diphenoquinones were determined, and are summarized in Table I. Only the spectrum of I⁵ and a portion of the spectrum of III⁹ have been previously reported.

The principal maximum in the visible is probably due to contributions, in the first excited state, from resonance structures of the type



Substituents in the 3,3',5,5'-positions apparently have only a slight effect on these principal contributing forms. The shift of 19 $m\mu$ (from 395 to 414 $m\mu$) when a hydrogen atom is replaced by a methyl group may be interpreted in terms of hyperconjugation involving the methyl groups, and this shift is only slightly different (to 420 $m\mu$) for the *t*-butyl group. Pianka, *et al.*,¹⁰ have interpreted the similar bathochromic shift on going from the 2,4-dinitrophenylhydrazone of formaldehyde to those of acetaldehyde and higher aldehydes¹¹ in a similar manner, and point out the possible generality of bathochromic and hypsochromic shifts on alkyl substitution. The main feature of the spectra of the diphenoquinones, however, is their similarity, and the relative independence of the nature of the substituent.

Experimental

Diphenoquinone (I).—To 5 g. of 4,4'-dihydroxydiphenyl¹² dissolved in 720 ml. of ether there was added 25 g. of activated⁸ lead dioxide. The mixture was shaken mechanically for about 30 minutes. After filtration, the lead dioxide residue containing I was extracted by refluxing for 15 minutes once with 1 l. and twice with 500 ml. of benzene. Cooling the combined extracts gave 1.69 g. of red crystalline I. Concentration of the mother liquors gave an additional 0.58 g. Additional product (0.40 g.) was precipitated from the mother liquors with ligroin, the gold crystalline modification of I being obtained. Recrystallization of the red crystals from benzene gave the gold form. The total yield was 2.67 g. (53.9%). The reaction time could be varied from 15 to 45 minutes without an appreciable effect on the yield.

*Anal.*¹³ Calcd. for C₁₂H₆O₂: C, 78.25; H, 4.38. Found: red form, C, 78.55; H, 4.39; gold form, C, 78.42; H, 4.60.

Spectra.—Chloroform was purified by the method of Fieser,¹⁴ and absolute alcohol was dried by distillation from calcium oxide. The spectra were determined with a Beckman model DU quartz spectrophotometer, using 1-cm. matched quartz cells. It should be noted that solutions of I in alcohol are unstable, and the spectrum must be determined rapidly. In chloroform I decomposes too rapidly for the determination of its spectrum. The same holds for alcoholic solutions of IV. Solutions of II and III in both solvents are stable.

(9) H. Hart and F. A. Cassis, *THIS JOURNAL*, **73**, 3179 (1951).

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(11) E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 499 (1945).

(12) R. Hirsch, *Ber.*, **22**, 335 (1889).

(13) Clark Microanalytical Laboratories, Urbana, Illinois.

(14) L. F. Fieser, *ref. 7*, p. 365.

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Phenolphthalol

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RECEIVED APRIL 19, 1952

By reduction of phenolphthalin (4',4''-dihydroxy-triphenylmethane-2-carboxylic acid) with sodium

amalgam, Baeyer¹ obtained a product melting at 190°, which he called phenolphthalol. He reported that this compound is oxidized to phenolphthalein by potassium ferricyanide. He also described a red, water-insoluble condensation product formed by treatment of phenolphthalol with concentrated sulfuric acid.

By reduction of phenolphthalin with lithium aluminum hydride, in this Laboratory, a compound which melted at 201° was obtained. This substance neither produced Baeyer's red product, nor did it yield phenolphthalein on oxidation. This phenolphthalol, 2-(4',4''-dihydroxybenzhydryl)-benzyl alcohol (I), gave a mono- as well as a triacetyl derivative, as would be expected from its formula.

Experimental

Phenolphthalol (I).—A three-necked flask fitted with a rubber-sleeved stirrer, an inlet tube for nitrogen, and a glass tube holding a 25 × 85 mm. glass thimble topped by a reflux condenser, was charged with 500 ml. of absol. ether and 3.0 g. of LiAlH₄. Into the thimble was placed 6.40 g. (0.02 mole) of phenolphthalin (m.p. 233–236°). After two hours of refluxing, the latter had dissolved. Stirring was continued for 16 hours at 36°. Then a mixture of 50 ml. of water and 35 ml. of concd. hydrochloric acid was carefully added and the ether layer extracted with 2 *N* sodium carbonate. Phenolphthalin (0.81–0.97 g.) was recovered from the extract. After evaporation of the ether, the solid was recrystallized from either water (1 g. in 750 ml.) or from 20% ethanol (1 g. in 110 ml.). The yield was 4.65–4.96 g. (76–81%); m.p. 201–202°.

The pure I, colorless needles, melts at 201.5–201.9° cor. It can be sublimed at 180° and 8 microns pressure.² It is very soluble in acetone or ethanol, soluble in ether, and insoluble in chloroform or benzene. Its solution in dilute alkali is colorless; a 0.001 molar solution in concd. sulfuric acid is of moderate orange color.

Anal. Calcd. for C₂₀H₁₈O₃: C, 78.42; H, 5.92; mol. wt., 306. Found: C, 78.59; H, 6.25; mol. wt., 292.³

When a solution of phenolphthalein in dilute acetic acid was treated with sodium amalgam according to Baeyer's procedure,¹ a crude product which melted at about 190° was obtained in very low yield. After several crystallizations from water it melted at 198–199° and proved to be identical with I.

Monoacetyl Derivative of I.—A mixture of 1.0 g. of I and 10 ml. of acetic acid was refluxed for one hour. The crude product was treated with 50 ml. of hot benzene and then filtered; the insoluble portion was I. Yellow crystals separated from the cooled filtrate. After further crystallizations from either benzene or chloroform, the pure monoacetate was obtained in the form of colorless crystals, m.p. 171.5–173.6° cor. It is soluble in dilute sodium hydroxide.

Anal. Calcd. for C₂₀H₂₀O₄: C, 75.84; H, 5.78; CH₃CO-, 12.3; mol. wt., 348. Found: C, 75.68; H, 5.75; CH₃CO-, 12.2; mol. wt., 329.³

Triacetyl Derivative of I.—A mixture of 1.0 g. of I, 2 ml. of acetic anhydride and a trace of sulfuric acid was heated for 30 minutes at 100°. The crude material was crystallized from 5 ml. of ethanol (1.29 g., 91%). The pure compound, obtained from methanol (1 g. in 3 ml.) or from ethanol (1 g. in 4 ml.) forms colorless crystals which melted at 104.8–105.6° cor.; it is insoluble in dilute alkali.

Anal. Calcd. for C₂₆H₂₄O₆: C, 72.21; H, 5.59; mol. wt., 432. Found: C, 71.88; H, 5.76; mol. wt., 410.³

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(2) M. H. Hubacher, *Ind. Eng. Chem., Anal. Ed.*, **15**, 448 (1943).

(3) Signer method, as described by E. P. Clark, *ibid.*, **13**, 820 (1941).

The Synthesis of Nitrogen-containing Ketones. II. Ketones Derived from 2-Picoline, Quinaldine and 2,6-Lutidine

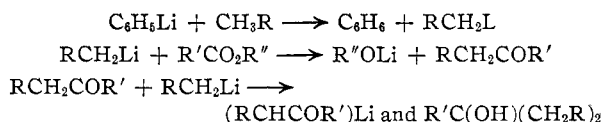
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RECEIVED MAY 21, 1952

In connection with an extensive program which is in progress in this Laboratory on the synthesis of potential chelating agents^{1–5} containing heterocyclic nuclei, we have been interested in developing general methods for the synthesis of heterocyclic ketones. To date progress has been made in the thiophene, furan and 2-picoline series.^{6–10}

The present report is concerned with further acylations of 2-picoline and the extension of the method recently described¹⁰ to the condensation of quinaldine and 2,6-lutidine with a number of esters. Of the three ketones described in this paper which were obtained by acylating 2-picoline, 2-pyridyl 2-picolyl ketone was previously prepared by Wibaut and de Jong¹¹ in 13% yield by the interaction of 2 lithiopicolyl with benzonitrile and hydrolyzing the resulting ketimine. Five of the quinaldyl ketones, prepared in our study, have also been synthesized earlier. The methods employed by the earlier workers involved the interaction of the sodium or potassium derivative of quinaldine (prepared from the tar base and either sodium or potassium amide) with the appropriate esters. Thus, the methyl, ethyl and isopropyl ketones were prepared in 17–36% yields by Weiss and Hauser¹²; while the phenyl and 2-furyl ketones have been reported by Bergstrom and Moffat¹³ in yields of 60–65% and 28%, respectively. Apparently only one acylated derivative of 2,6-lutidine has been reported. Thus, de Jong and Wibaut¹⁴ have prepared 2-methyl-6-phenacylpyridine in 30% yield by the ketimine synthesis.

The method employed in our syntheses may be summarized by the following general equations where CH₃R represents 2-picoline, quinaldine or 2,6-lutidine.



Our results are summarized in Table I. It may be seen that good to high yields of condensation products were obtained in all cases. While the present acylations of 2-picoline and quinaldine gave only ketonic products, the acylation of 2,6-

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- (7) R. Levine, J. V. Heid and M. W. Farrar, *THIS JOURNAL*, **71**, 1207 (1949).
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