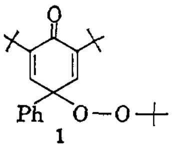
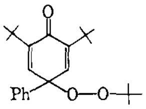
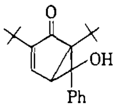


1

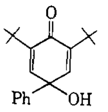
One product isolated from the reaction mixture was thought to be 2 (on the basis of spectral data). This was shown to be incorrect later, but it prompted the investigation of 3[2] as a possible precursor to 2. The photolysis of 3 itself is of interest since (a) it is a dienone with bulky *ortho* substituents, (b) in view of the work of Yang[3] it would be of importance to establish whether the methyl hydrogens participate in intramolecular H-transfer to give cyclobutanol derivatives, and (c) 3 is an example of a cross-conjugated dienone having groups other than carbon attached directly in the 4-position.[4]



1

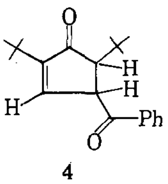


2



3

The photolysis of 3 (0.5% solutions in dioxane containing a small amount of water) was carried out in Pyrex with a Hanovia utility lamp at 22 ± 2° until most of 3 had been consumed. Column chromatography and fractional crystallization gave a crystalline solid 4, m.p. 157.0–158.2°, isomeric with 3, $C_{20}H_{26}O_2$. The ultraviolet spectrum (in methanol) of 4 showed absorption at 318 mμ (ϵ 249) and strong end absorption at 223 mμ (cyclopentenone), as well as absorption at 328 (249), 277 (1440), and 243 (22,400) (benzoyl group); strong infrared bands were observed at 1691 (conjugated carbonyl), 1681 (benzoyl–carbonyl), and 1007 cm.$^{-1}$, as well as aromatic bands constituent with mono-substitution. The n.m.r. spectrum showed peaks at τ 8.99 and 8.84 (*t*-butyl groups), a doublet (J = 2.5 c.p.s.) centered at 7.05 (tertiary H), a triplet at 5.48 (PhCO–CH), a doublet (J = 3 c.p.s.) at 2.88 (O=C—C=C—H), and aromatic peaks in the 2.46–1.92 region. Peak areas were in the approximate ratios of 9:9:1:1:1:5. Compound 4 formed a mono-2,4-dinitrophenyl hydrazone (sharp carbonyl absorption at 1691 cm.$^{-1}$), m.p. 166.0–167.4°, $C_{26}H_{30}N_4O_5$. These data established the structure of 4 as a cyclopentenone derivative.



4

The yield of 4 was about 20%. A second crystalline compound, m.p. 110.8–11.6°, also isomeric with 3, was isolated in very low yield; sufficient material for full characterization has not been accumulated.

No evidence for 2 or other fractions containing hydroxyl absorption has been obtained. The occurrence of 2 as an intermediate would have been of interest, since it could give rise to 4 *via* a cyclopropanol ring opening of the type observed by DePuy,[5] although DePuy has recently reported[6] that this reaction is probably not free radical in nature. By employing the polar concept of product control in photochemical reactions,[7] the rearrangement of 3 to 4 *via* 2 can be rationalized. The generality of the reaction is under exploration.

Experimental[8]

The starting material 3 was prepared according to Müller, *et al.*,[2] m.p. 140.2–141.0°. Eastman White Label dioxane was passed over alumina just before use. The solution (containing *ca.* 5% water) was flushed 30 min. with oxygen-free N_2 before irradiation commenced. The course of the reaction was followed by thin layer chromatography (silica gel G). When most or all of 3 had been consumed, the solvent was removed by vacuum distillation at about 30°. The viscous residue was treated with hexane (or cyclohexane) to give a small crop of 4 or was taken up in ether, dried, and, after removal of the ether, chromatographed on Woelm III neutral alumina from hexane. Two recrystallizations of the first fraction from hexane–chloroform gave 4, m.p. 157.0–158.2°; yields varied somewhat (10–25%) depending on work-up.

Anal. Calcd. for $C_{20}H_{26}O_2$: C, 80.40; H, 8.78. Found: C, 80.28; H, 8.47; mol. wt., 298.4 (Rast, 251). Calcd. for $C_{26}H_{30}N_4O_5$: C, 65.22; H, 6.32; N, 11.70. Found: C, 65.14; H, 6.49; N, 11.57.

Acknowledgment.—The authors wish to thank Dr. Michael Gianni for his help with the n.m.r. spectrum and the Petroleum Research Fund (Grant 1156-A4) for financial assistance.

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[2] E. Müller, A. Schick, and K. Scheffler, *Chem. Ber.*, **92**, 474 (1959).

[3] N. C. Yang and D. H. Yang, *J. Am. Chem. Soc.*, **80**, 2913 (1958).

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(5) C. H. DePuy, G. H. Dappen, and J. W. Hauser, *ibid.*, **83**, 3156 (1961).

(6) C. H. DePuy and F. W. Breitbeil, *ibid.*, **85**, 2176 (1963).

(7) O. L. Chapman, A. I. Dutton, and P. Fitton, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., 1962, p. 88Q; *cf.*, W. A. Noyes, G. S. Hammond, and T. N. Pitts, "Advances in Photochemistry," Vol. 1, John Wiley and Sons, Inc., New York, N. Y., 1963, p. 323.

(8) All melting points are uncorrected. Analyses are by Galbraith Laboratories, Knoxville 21, Tenn. The n.m.r. spectrum was obtained on a Varian A-60 (using tetramethylsilane as internal standard).

The Structure of 1,3-Naphthalenediol Anion

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Although the ketone form of phenols is frequently postulated to explain certain of their reactions, direct observations of such ketone–enol interconversions are scarce. Among the few examples of the presence of the ketone form are the partial isomerization of 1,4-naphthalenediols in the molten state[2,3] and the equili-

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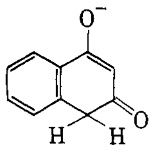
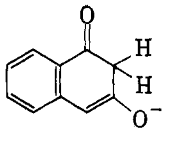
(1) To whom inquiries should be addressed.

(2) D. B. Bruce and R. H. Thomson, *J. Chem. Soc.*, 2759 (1952).

(3) *Cf.* also the existence of leucoquinizarin, a 1,4-naphthalenediol, in the ketone form: S. M. Bloom and R. F. Hutton, *Tetrahedron Letters*, 1993 (1963).



I



II

bration of anthrol with anthrone.[4,5] We have now found that the monoanion of 1,3-naphthalenediol exists in the tautomeric form, I or II.

Conclusive evidence for the ketone–enolate structure comes from n.m.r. studies. A 0.5 *M* aqueous solution[6] of 1,3-naphthalenediol has the spectrum shown in the upper part of Fig. 1, where the AB system near 6.5 p.p.m. is due to H-2 and H-4; as the solution is neutralized the area of these peaks decreases and two new peaks appear at higher field. The spectrum of a 90% neutralized solution[6] (*ca.* 0.8 *M*) is shown in the lower part of Fig. 1, where the residual AB system, now at slightly higher field, is still apparent. When 1 equiv. of base has been added, the AB system can no longer be detected and the area ratio of the aromatic multiplet and the peaks near 5.33 and 3.08 p.p.m. is 4:1:2, in agreement with either I or II. After acidification the spectrum of unchanged naphthalenediol is obtained and naphthalenediol can also be isolated. When the spectrum of the anion is determined in D_2O only the four aromatic hydrogens of the nonoxygenated ring are discernible so that both H-4 and H-2 exchange rapidly.[7] This implies that sp^3 centers can be formed at both C-2 and C-4; that is, both tautomers could be present.

That there is a preponderance of one tautomer, probably I, is shown by the following considerations. Measurements of the chemical shifts of the vinyl and the methylene hydrogens in solutions 0.4 to 0.05 *M* anion concentration lead to extrapolated values of 5.50 and 3.66 p.p.m.[8] at infinite dilution. In the *anion* of acetyl acetone the vinyl hydrogen, which is in an environment similar to that of the vinyl hydrogen in I, absorbs at 5.24 p.p.m.[9] Tautomer I, in which delocalization of the negative charge does not disrupt the aromaticity of the other ring, is also preferred on theoretical grounds. Further, it may be noted that if the interconversion of tautomers I and II were not slow relative to the n.m.r. measurement, then one should observe either a single line, due to both the vinyl and methylene groups (in the case of an intramolecular interconversion), or a line "coalesced" with the water peak (in the more likely case of proton transfer involving water). Therefore the interconversion of tautomers I and II must be slow compared to the n.m.r. measurement. The fact that the spectrum shows only one set of lines for the vinyl and the methylene hydrogens indicates that one tautomer is present in much greater concentration than the other.

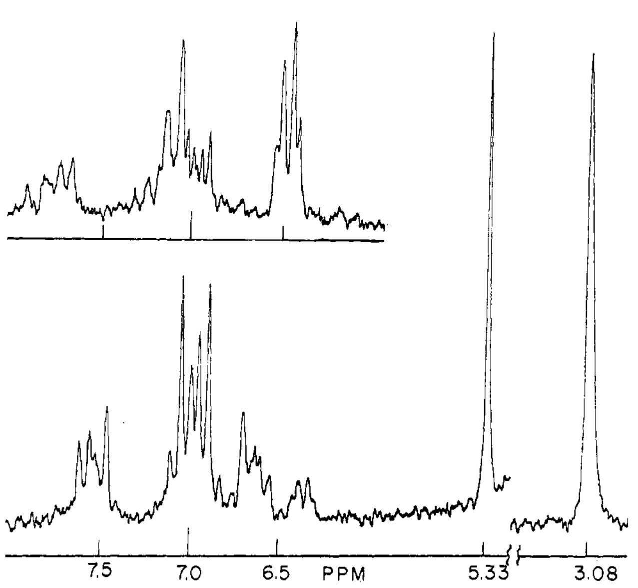
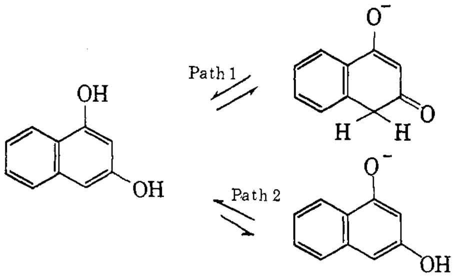


Fig. 1.—Proton resonance spectra of aqueous solutions of 1,3-naphthalenediol (upper curve) and of 90% neutralized 1,3-naphthalenediol (lower curve) at 60 Mc., and, relative to the solvent (water), peak = 4.74 p.p.m. at 27.5°.

The acidity constant of 1,3-naphthalenediol also reflects its unusual properties. Phenol and 1-naphthol have very similar pK_a values, 9.95 and 9.85,[10] respectively, and, since the effects of substituents on the pK_a are approximately additive,[10] one would expect the pK_a of 1,3-naphthalenediol to be similar to that of resorcinol, namely, 9.44.[10] It is, in fact, 7.35.[11] The *observed* acidity constant is for the dissociation of the aromatic compound to the ketone–enolate (path 1) whereas the *predicted* acidity constant is for the dissociation to the phenolate ion (path 2). The difference between the two values reflects the difference in free energy of the two solvated anions and is about 2.5 kcal./mole.



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[4] See, for example, K. Nukada and Y. Bansho, *Repts. Gov. Chem. Ind. Res. Inst. Tokyo*, **49**, 15 (1954); *Chem. Abstr.*, **50**, 11,304e (1956); K. H. Meyer, *Ann.*, **379**, 37 (1911); and K. H. Meyer and A. Sander, *ibid.*, **396**, 133 (1913).

[5] The equilibration of 4-phenylazo-1-naphthol with the tautomeric phenylhydrazone [see, for example, E. Fischer and Y. F. Frei, *J. Chem. Soc.* 3159 (1959)] and of certain *p*-nitrosophenols with the tautomeric quinone monoximes [L. A. Cohen and W. M. Jones, *J. Am. Chem. Soc.*, **85**, 3397 (1963)], and the existence in the ketonic form of imino derivatives of certain 2-acyl-1-naphthols or 1-acyl-2-naphthols [G. O. Dudek, *ibid.*, **85**, 694 (1963)] are not directly analogous examples since here changes other than the enol-ketone conversion take place also.

[6] The position of all peaks (and the splitting pattern) is strongly concentration dependent; *e.g.*, at higher concentration the AB system coalesces to a single peak at higher field.

[7] For exchange of nuclear hydrogens in other compounds derived from resorcinols, see E. S. Hand and R. M. Horowitz, *J. Am. Chem. Soc.*, **86**, 2084 (1964). In this compound the exchange also occurs in the absence of base.

[8] Relative to the solvent (water) peak = 4.74 ± 0.02 p.p.m. at 27.5° or external tetramethylsilane (TMS) in carbon tetrachloride = 0. The usual internal standard, sodium 3-(trimethylsilyl)propane sulfonate (DDS), was unsuited since its methyl absorption was shifted upfield in the presence of the naphthalene derivative. The peaks of some other materials were also affected to varying extents. These results will be published elsewhere.

[9] Relative to the solvent (water) peak = 4.74 ± 0.02 p.p.m., internal DDS, or external TMS in carbon tetrachloride = 0. The chemical shift of this peak does not change on dilution.

[10] H. C. Brown, D. H. McDaniel, and O. Häfliger, in "Determination of Organic Structures by Physical Methods," E. A. Braude and F. C. Nachod, Ed., Academic Press, New York, N. Y., 1955, p. 567.

[11] Determined in aqueous solution by potentiometric titration or measurement of the pH of a half-neutralized solution. In the presence of potassium chloride to give ionic strength = 0.5, the pK_a = 7.22.

Of interest also is the very recent report[12] that the *dianion* of phloroglucinol has a ketone structure while the monoanion appears to exist exclusively as the phenolate anion.

Acknowledgment.—We wish to thank Professor T. Cohen for helpful discussions.

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Methylation of Pyrrylmagnesium Bromide[1]

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In a recent study, Skell and Bean have shown that the alkylation of pyrrylmagnesium bromide (**1**) with a series of alkyl halides yields the isomeric 2- and 3-alkylpyrroles and polyalkylpyrroles as major products.[2] These findings confirmed the original report of Oddo[3] and refuted certain subsequent claims[4] regarding the nature of the products arising from the alkylation of **1**.[5] Skell and Bean employed only methyl bromide and tosylate as methylating agents for **1**; analysis of products was achieved by infrared analysis of distillation fractions.[2] The yields of 2-methyl- (**2**) and 3-methylpyrrole (**3**) and the conversion of pyrrole were low in these studies. Since the direct methylation of **1** represents an experimentally simple one-step synthetic entry to **2** and **3**, a reinvestigation of the methylation of **1** with methyl iodide, dimethyl sulfate, trimethyl phosphate, and methyl tosylate has been carried out under conditions different from those employed by Skell and Bean in an attempt to obtain synthetically useful yields of **2** and **3**. Product identification and analyses have been carried out by gas–liquid chromatography. The results obtained in this study are similar to those of Skell and Bean[2] with regard to both yields of **2** and **3** and utilization of **1**.

The alkylation of **1** with equimolar quantities of each of the four alkylating agents was carried out in refluxing ether (normal reaction period of 22 hr.); the reaction mixture was quenched under neutral conditions (deoxygenated water at 15°). Quenching by the use of ice and sulfuric acid[3] or aqueous ammonium chloride[6] gave poor product recovery and extensive formation of tars, presumably by the acid-catalyzed polymerization of pyrroles. The results of these methylation experiments are summarized in Table I.

Product identification and reaction mixture analyses were carried out by gas–liquid chromatography on a Carbowax 20M column, programming the column temperature from 50 to 150°. Under these conditions, pyrrole, N-methylpyrrole, **2** and **3** could be separated cleanly; each of these materials was identified by comparison of its g.l.c. behavior with that of an authentic sample and by collection of samples on elution and comparison with authentic materials. Further alkylated products (A and B, Table I) were not identified, but were separated cleanly by the g.l.c. method. Products A and B were shown not to be either 2,4- or 2,5-dimethylpyrroles by comparison of g.l.c. behavior. The authentic dimethylpyrroles had retention times slightly shorter than that of A; because of the similarity of retention times, A and B are assumed to be dimethylpyrroles or pyrrolenines. A third unidentified minor product (C) was also formed in these alkylations and was resolved cleanly and probably represents a higher methylated structure since an increase in column temperature was required for its elution. Other materials were eluted following C, but only as unresolved smears.

Methylation of 2-methylpyrrylmagnesium bromide with methyl iodide under the standard conditions of Table I led to extensive methylation (30% recovery of **2**); both compounds A and B were present as minor reaction products. Attempted methylation of 2,5-dimethylpyrrylmagnesium bromide under the standard conditions was unsuccessful; an almost quantitative recovery of the starting pyrrole was obtained. Under different reaction conditions, Johnson has observed the methylation of this Grignard reagent; 2,3,4,5-tetramethylpyrrole and tetramethylpyrrolenines were the major products.[6]

An examination of the results presented in Table I shows that the general conclusions of Skell and Bean[2] have been substantiated by this study. The major products of the reaction are **2** and **3**, obtained in ratios (**2** to **3**) of 1.3 to 3.1. With the exception of trimethyl phosphate which shows little selectivity, alkylation of the 2-position of **1** is favored by a factor of at least two. In contrast to the results of Skell and Bean[2] and earlier workers,[3,4] minor amounts of N-methylpyrrole were obtained; however, the analytical technique employed by these workers probably would not have allowed the detection of such minor amounts of material. Although the formation of the N-methylated product has not been observed previously, some degree of alkylation at this position might be expected since **1** has been shown to exist as either an N–MgX structure or a resonance-stabilized anion with the negative charge distributed between carbon and nitrogen.[7] In contrast, the N-alkylation of the alkali metal derivatives of pyrrole is well known.[8] Additionally, significant amounts of the higher methylated species A and B are also formed. The formation of A and B in the methylation of 2-methylpyrrylmagnesium bromide indicates these materials to possess a minimum of one 2-methyl group.

The observed increase in methylating ability [$CH_3I < (CH_3)_3PO_4 < (CH_3)_2SO_4 \cong CH_3OTs$] of the reagents studied follows the general trend observed for their reactivity toward Grignard reagents and carbanions.[9] Relatively little use has been made previously of the alkylating ability of trimethyl phosphate in Grignard

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(1) This study was supported in part by a grant from the Health Research and Services Foundation.

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(5) For a summary of references regarding the alkylation of **1**, see ref. 2.

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(7) M. G. Reinecke, H. W. Johnson, and J. F. Sebastian, *J. Am. Chem. Soc.*, **85**, 2859 (1963).

(8) P. A. Cantor and C. A. Vanderwerf, *ibid.*, **80**, 970 (1958).

(9) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954, Chapters XVI and XX; C. M. Suter and H. L. Gerhard, *J. Am. Chem. Soc.*, **57**, 107 (1935); J. M. Conia, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **24**, 43 (1963).