

Anal. Calcd. for $C_{29}H_{32}O_6N_2S_2 \cdot 5H_2O$: H_2O , 14.13. Found: H_2O , 14.33.

All of the water was lost below 160° . The free acid II did not have a sharp melting point but decomposed with evolution of much gas when heated above 350° . Electro-metric titration (glass electrode) with barium hydroxide showed the equivalence point for neutralization of both sulfonic acid groups to be pH 8.4. Solutions of the acid II could be titrated with phenol red as indicator.

On exposure to light with wave length of 2537 \AA . an aqueous solution of the dye cyanide (II) developed a blue color, but much more slowly than do alcoholic solutions of the basic dye cyanides. Spectroscopic examination of the irradiated solution showed the absorption band of xylene blue VS and also a new absorption band at longer wave lengths.

Xylene Blue AS Cyanide (III).—Xylene blue AS (Colour Index No. 673) was commercially available under several trade names. The starting product used in this work was Calcoacid Blue AX Double. This was identified by its manufacturer¹⁰ as Colour Index No. 714 but proved on examination to be No. 673.

To 25 g. of the dye in 150 ml. of hot water was added 9 g. of 95% sodium cyanide, and the solution in a pressure bottle

(10) American Cyanamid Company, Calco Chemical Division, Bound Brook, New Jersey.

was heated in a boiling water-bath for 1 hour. After cooling and standing overnight the precipitated sodium salt of the dye cyanide was collected on a filter. The yield of crude salt was 16.8 g.

The free acid III was precipitated from a solution of 15 g. of the crude sodium salt in 400 ml. of water by addition of 22.5 ml. of 2 *N* hydrochloric acid. After standing for several days 13 g. of acid was collected. This was recrystallized from 1000 times its weight of water.

*Anal.*⁷ Calcd. for $C_{28}H_{37}O_6N_2S_2$: N, 6.04; S, 9.22. Found: N, 6.16; S, 9.96, 9.18, 9.40.

The product did not have a sharp melting point, but when heated above 270° gradually decomposed with evolution of gas.

Electrometric titration with a glass electrode gave the equivalence point as pH 8.0 for the neutralization of both sulfonic acid groups.

On neutralization with barium hydroxide the free acid formed a slightly-soluble barium salt.

On exposure to light of wave length 2537 \AA . aqueous solutions of xylene blue AS cyanide (III) slowly developed a green color. Spectroscopic examination showed the absorption band of xylene blue AS and also a new band in the violet.

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[CONTRIBUTION FROM LOS ALAMOS SCIENTIFIC LABORATORY, UNIVERSITY OF CALIFORNIA]

2,5-Diaryloxazoles and 2,5-Diaryl-1,3,4-oxadiazoles

BY F. NEWTON HAYES, BETTY S. ROGERS AND DONALD G. OTT

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A number of previously unreported 2,5-diaryloxazoles and 2,5-diaryl-1,3,4-oxadiazoles have been prepared by cyclization of 1,4-diaryl-2-aza-1,4-diketones and 1,2-diaroylhydrazines.

The discovery that 2-phenyl-5-(4-biphenyl)-oxazole¹ functioned as an efficient scintillation solute prompted the synthesis of a large number of 2,5-diaryloxazoles and related compounds which might possess certain desired characteristics for organic solution scintillators.² Until this discovery was made *p*-terphenyl was the only efficient organic scintillation solute known.

A convenient abbreviation system was originated in the course of this investigation and has since become commonly used by research workers, as well as commercial organizations, in the organic scintillator field. This system uses the letter P for phenyl, B for 4-biphenyl, N for naphthyl, O for oxazole, D for oxadiazole, and so forth, with M signifying a methyl *p*-toluenesulfonate quaternary salt. Thus, for example, 2-(1-naphthyl)-5-(4-biphenyl)-oxazole becomes α NBO, and 2-(4-biphenyl)-5-phenyloxazole is BPO. The convention of giving first the 2-substituent, secondly the 5-substituent, and then the ring system is not utilized with the more complicated structures, e.g., 5,5'-diphenyl-2,2'-bioxazoly1 (POOP) or 1,4-di-

[2-(5-phenyl-1,3,4-oxadiazoly1)]-benzene (PDP-DP). For such compounds the abbreviations are derived from the order in which the rings appear in the structure.

For the most part, the new compounds listed in the tables were prepared by known methods. The oxazoles (Table I) resulted from cyclization of 2-aza-1,4-diketones (Fig. 1). POPOP, BOPOP and POOP were prepared by an extension of the method to difunctional acid chlorides. The general procedure for dissolving a 2-aza-1,4-diketone in sulfuric acid and precipitating with water to give the oxazole³ is a simple reaction to execute but fails to yield the desired product in certain cases. This failure occurred in the attempted preparations of 2-(3,4-methylenedioxy)-5-phenyloxazole, POPOP, POOP, and in all cases involving the 4-biphenyl group. Each of these compounds was successfully prepared by refluxing its amide with phosphorus oxychloride, a method which is now used exclusively.

Phosphorus oxychloride was also employed in the preparation of the 2,5-diaryl-1,3,4-oxadiazoles (Table II) from 1,2-diaroylhydrazines (Fig. 2).

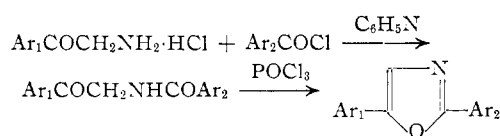


Fig. 1.—Synthesis of 2,5-diaryloxazoles.

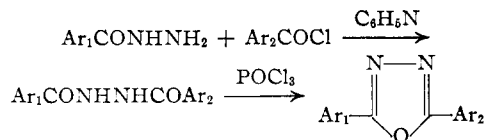


Fig. 2.—Synthesis of 2,5-diaryl-1,3,4-oxadiazoles.

(1) F. N. Hayes, L. C. King and D. E. Peterson, *THIS JOURNAL*, **74**, 1108 (1952).

(2) The application of these compounds as organic scintillators is being reported elsewhere.

The intermediate 2-aza-1,4-diketones and 1,2-diaroylhydrazines usually could be satisfactorily

(3) J. Lister and R. Robinson, *J. Chem. Soc.*, 1297 (1912).

TABLE I
2,5-DIARYLOXAZOLES

| Ar ₁ | Ar ₂ | Formula | M.p., °C. | Carbon | | Hydrogen | | Nitrogen | | M.p., °C. | Corresponding 2-aza-1,4-diketone Nitrogen, % | |
|---|---|---|-----------|--------|-------|----------|-------|----------|-------|-------------|--|-------|
| | | | | Calcd. | Found | Calcd. | Found | Calcd. | Found | | Calcd. | Found |
| C ₆ H ₅ | 2-FC ₆ H ₄ | C ₁₈ H ₁₆ FNO | 84-85 | 75.30 | 75.72 | 4.21 | 4.41 | 5.86 | 5.68 | 116-117 | 5.45 | 5.10 |
| C ₆ H ₅ | 3-FC ₆ H ₄ | C ₁₈ H ₁₆ FNO | 69-70 | 75.30 | 75.55 | 4.21 | 4.22 | 5.86 | 5.71 | 128-129 | 5.45 | 5.23 |
| C ₆ H ₅ | 4-FC ₆ H ₄ | C ₁₈ H ₁₆ FNO | 81-82 | 75.30 | 75.56 | 4.21 | 4.35 | 5.86 | 5.53 | 134-135 | 5.45 | 5.30 |
| C ₆ H ₅ | 4-ClC ₆ H ₄ | C ₁₈ H ₁₆ ClNO | 115-116 | 70.46 | 70.77 | 3.94 | 3.98 | 5.48 | 5.37 | 148-148.5 | 5.12 | 5.55 |
| C ₆ H ₅ | 2,4-Cl ₂ C ₆ H ₃ | C ₁₈ H ₁₄ Cl ₂ NO | 116-116.5 | 62.09 | 62.62 | 3.13 | 3.46 | 4.83 | 4.98 | 122.5-123 | 4.55 | 4.65 |
| C ₆ H ₅ | 3,4-Cl ₂ C ₆ H ₃ | C ₁₈ H ₁₄ Cl ₂ NO | 124.5-125 | 62.09 | 61.86 | 3.13 | 3.30 | 4.83 | 4.77 | 146.5-147 | 4.55 | 4.48 |
| C ₆ H ₅ | 2-Br ₂ C ₆ H ₃ | C ₁₈ H ₁₄ Br ₂ NO | 71-72 | 60.02 | 60.54 | 3.36 | 3.77 | 4.67 | 4.74 | 115.5-116.5 | 4.40 | 4.21 |
| C ₆ H ₅ | 3-Br ₂ C ₆ H ₃ | C ₁₈ H ₁₄ Br ₂ NO | 86-87 | 60.02 | 60.41 | 3.36 | 3.87 | 4.67 | 4.80 | 129-130 | 4.40 | 4.17 |
| C ₆ H ₅ | 4-Br ₂ C ₆ H ₃ | C ₁₈ H ₁₄ Br ₂ NO | 115-116 | 60.02 | 59.64 | 3.36 | 3.58 | 4.67 | 4.70 | 164-165 | 4.40 | 4.31 |
| C ₆ H ₅ | 2-IC ₆ H ₄ | C ₁₈ H ₁₆ INO | 78.5-79.5 | 51.89 | 52.09 | 2.90 | 3.06 | 4.04 | 3.87 | 111.5-112.4 | 3.84 | 3.85 |
| C ₆ H ₅ | 3-IC ₆ H ₄ | C ₁₈ H ₁₆ INO | 112-113 | 51.89 | 52.51 | 2.90 | 3.02 | 4.04 | 4.01 | 146-147 | 3.84 | 3.64 |
| C ₆ H ₅ | 4-IC ₆ H ₄ | C ₁₈ H ₁₆ INO | 130-131 | 51.89 | 51.90 | 2.90 | 3.14 | 4.04 | 3.61 | 163-165 | 3.84 | 3.72 |
| C ₆ H ₅ | 2-CH ₃ OC ₆ H ₄ | C ₁₈ H ₁₈ NO ₂ | 145-146 | 76.47 | 76.32 | 5.22 | 5.11 | 5.57 | 5.47 | 102-103 | 5.20 | 4.83 |
| C ₆ H ₅ | 3-CH ₃ OC ₆ H ₄ | C ₁₈ H ₁₈ NO ₂ | 79-80 | 76.47 | 76.44 | 5.22 | 5.28 | 5.57 | 5.34 | 80-81 | 5.20 | 4.98 |
| C ₆ H ₅ | C ₆ H ₁₁ | C ₁₈ H ₁₇ NO | 87 | 79.26 | 79.41 | 7.54 | 7.51 | 6.16 | 6.01 | 113-114 | 5.71 | 5.45 |
| C ₆ H ₅ | 2-C ₁₀ H ₇ | C ₁₉ H ₁₈ NO | 110-111 | 84.11 | 84.06 | 4.83 | 4.94 | 5.16 | 5.41 | 148 | 4.84 | 4.85 |
| C ₆ H ₅ | 4-C ₆ H ₅ C ₆ H ₄ | C ₂₁ H ₁₈ NO | 112-113 | 84.82 | 84.77 | 5.09 | 4.85 | 4.71 | 4.62 | 181-182 | 4.44 | 4.65 |
| C ₆ H ₅ | 2-Thienyl | C ₁₈ H ₉ NOS | 67-68 | 68.70 | 68.90 | 3.99 | 4.00 | 6.16 | 6.30 | 140-141 | 5.71 | 5.58 |
| C ₆ H ₅ | 2-Furyl | C ₁₈ H ₉ NO ₂ | 68-69 | 73.92 | 73.75 | 4.30 | 4.19 | 6.63 | 6.56 | 138 | 6.11 | 6.06 |
| C ₆ H ₅ | 2-(5-Phenyloxazolyl) | C ₁₈ H ₁₂ N ₂ O ₂ | 242-243 | 74.99 | 75.38 | 4.20 | 4.38 | 9.72 | 9.38 | 198-200 | 8.64 | 8.50 |
| 4-C ₆ H ₅ C ₆ H ₄ | 4-C ₆ H ₅ C ₆ H ₄ | C ₂₇ H ₁₉ NO | 232-233 | 86.84 | 86.98 | 5.13 | 5.19 | 3.75 | 3.82 | 257-259 | 3.58 | 3.97 |
| 1-C ₁₀ H ₇ | 1-C ₁₀ H ₇ | C ₂₃ H ₁₆ NO | 90-91 | 85.96 | | 4.71 | | 4.36 | 4.21 | 144-145 | 4.13 | 4.18 |
| 4-C ₆ H ₅ C ₆ H ₄ | 1-C ₁₀ H ₇ | C ₂₃ H ₁₇ NO | 163-164 | 86.43 | 86.44 | 4.93 | 5.07 | 4.03 | 4.04 | 131-132 | 3.83 | 3.64 |
| 2-C ₁₀ H ₇ | 1-C ₁₀ H ₇ | C ₂₃ H ₁₈ NO | 127-128 | 85.96 | 85.80 | 4.71 | 4.80 | 4.36 | 4.26 | 140-141 | 4.13 | 3.73 |
| 2-C ₁₀ H ₇ | 2-C ₁₀ H ₇ | C ₂₃ H ₁₈ NO | 187-188 | 85.96 | 86.12 | 4.71 | 4.74 | 4.36 | 4.19 | 203-204 | 4.13 | 4.16 |
| 4-C ₆ H ₅ C ₆ H ₄ | 2-C ₁₀ H ₇ | C ₂₃ H ₁₇ NO | 197-198 | 86.43 | 86.10 | 4.93 | 4.98 | 4.03 | 3.78 | 204-205 | 3.83 | 3.63 |
| 2-C ₁₀ H ₇ | 4-CH ₃ OC ₆ H ₄ | C ₂₁ H ₁₈ NO ₂ | 114-115 | 79.71 | 79.86 | 5.02 | 5.14 | 4.65 | 4.50 | 154-155 | 4.39 | 4.13 |
| 4-C ₆ H ₅ C ₆ H ₄ | 4-CH ₃ OC ₆ H ₄ | C ₂₂ H ₁₇ NO ₂ | 166-167 | 80.71 | 80.84 | 5.23 | 5.27 | 4.28 | 4.37 | 185-187 | 4.06 | 3.98 |
| | Ar ₁ = C ₆ H ₅ | C ₂₄ H ₁₆ N ₂ O ₂ | 237-238 | 79.10 | 79.35 | 4.43 | 4.45 | 7.69 | 7.93 | 262-268 | 7.00 | 6.87 |
| | Ar ₂ = C ₆ H ₄ C ₆ H ₅ | C ₂₆ H ₂₄ N ₂ O ₂ | 292-294 | 83.70 | 83.55 | 4.68 | 4.67 | 5.42 | 5.33 | 250 | 5.07 | 4.63 |

^a Melting points taken on a Fisher-Johns melting point block. Microanalyses by Micro-Tech Laboratories, Skokie, Ill.

TABLE II
2,5-DIARYL-1,3,4-OXADIAZOLES

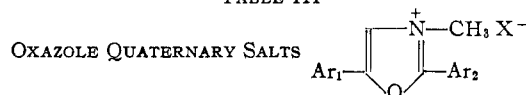
| Ar ₁ | Ar ₂ | Formula | M.p., °C. | Carbon, % | | Hydrogen, % | | Nitrogen, % | |
|---|---|---|-----------|-----------|-------|-------------|-------|-------------|-------|
| | | | | Calcd. | Found | Calcd. | Found | Calcd. | Found |
| C ₆ H ₅ | 2-Furyl | C ₁₂ H ₈ N ₂ O ₂ | 103-103.5 | 67.92 | 67.83 | 3.80 | 3.62 | 13.20 | 12.98 |
| C ₆ H ₅ | 2-Thienyl | C ₁₂ H ₈ N ₂ OS | 117-118 | 63.14 | 63.34 | 3.53 | 3.71 | 12.27 | 12.15 |
| C ₆ H ₅ | 4-C ₆ H ₅ C ₆ H ₅ | C ₂₀ H ₁₄ N ₂ O | 166-167 | 80.52 | 80.54 | 4.73 | 4.67 | 9.39 | 9.26 |
| C ₆ H ₅ | 1-C ₁₀ H ₇ | C ₁₈ H ₁₂ N ₂ O | 120 | 79.39 | 79.63 | 4.44 | 4.63 | 10.29 | 9.98 |
| C ₆ H ₅ | 2-C ₁₀ H ₇ | C ₁₈ H ₁₂ N ₂ O | 122-124 | 79.39 | 79.73 | 4.44 | 4.81 | 10.29 | 10.07 |
| 4-CH ₃ OC ₆ H ₄ | 2-C ₁₀ H ₇ | C ₂₀ H ₁₄ N ₂ O ₂ | 148 | 75.48 | 75.67 | 4.67 | 4.65 | 9.27 | 9.06 |
| 4-CH ₃ OC ₆ H ₄ | 1-C ₁₀ H ₇ | C ₂₀ H ₁₄ N ₂ O ₂ | 142-143 | 75.48 | 75.55 | 4.67 | 4.64 | 9.27 | 9.11 |
| 4-CH ₃ OC ₆ H ₄ | 4-C ₆ H ₅ C ₆ H ₄ | C ₂₁ H ₁₆ N ₂ O ₂ | 155 | 76.81 | 76.94 | 4.91 | 4.89 | 8.53 | 8.21 |
| 4-IC ₆ H ₄ | 4-IC ₆ H ₄ | C ₁₄ H ₈ I ₂ N ₂ O | 276 | 35.47 | 36.85 | 1.70 | 1.98 | 5.91 | 5.94 |
| 4-FC ₆ H ₄ | 4-FC ₆ H ₄ | C ₁₄ H ₈ F ₂ N ₂ O | 200-202 | 65.12 | 64.85 | 3.12 | 3.06 | 10.85 | 10.90 |
| 4-ClC ₆ H ₄ | 4-ClC ₆ H ₄ | C ₁₄ H ₈ Cl ₂ N ₂ O | 242-243 | 57.75 | 57.76 | 2.77 | 2.96 | 9.62 | 10.00 |
| 4-CH ₃ OC ₆ H ₄ | 4-CH ₃ OC ₆ H ₄ | C ₁₆ H ₁₄ N ₂ O ₃ | 161-162 | 68.07 | 67.76 | 5.00 | 4.91 | 9.92 | 10.18 |
| 2-Furyl | 2-Furyl | C ₁₀ H ₆ N ₂ O ₃ | 141-142 | 59.41 | 59.50 | 2.99 | 2.90 | 13.86 | 13.67 |
| 2-Thienyl | 2-Thienyl | C ₁₀ H ₆ N ₂ OS ₂ | 117-118 | 51.26 | 51.58 | 2.58 | 2.70 | 11.96 | 11.62 |
| ω-Styryl | ω-Styryl | C ₁₈ H ₁₄ N ₂ O | 151-152 | 78.81 | 79.13 | 5.14 | 5.48 | 10.21 | 10.10 |
| 1-C ₁₀ H ₇ | 1-C ₁₀ H ₇ | C ₂₂ H ₁₄ N ₂ O | 175-177 | 81.97 | 82.31 | 4.38 | 4.34 | 8.69 | 8.51 |
| 2-C ₁₀ H ₇ | 2-C ₁₀ H ₇ | C ₂₂ H ₁₄ N ₂ O | 187-189 | 81.97 | 81.75 | 4.38 | 4.38 | 8.69 | 8.57 |
| 4-C ₆ H ₅ C ₆ H ₄ | 4-C ₆ H ₅ C ₆ H ₄ | C ₂₇ H ₁₈ N ₂ O | 229-230 | 83.40 | 83.21 | 4.85 | 4.90 | 7.48 | 7.26 |
| Ar ₃ = C ₆ H ₅ | | C ₂₂ H ₁₄ N ₄ O ₂ | 308-309 | 72.12 | | 3.85 | | 15.29 | 14.78 |

^a Melting points taken on a Fisher-Johns melting point block. Microanalyses by Micro-Tech Laboratories, Skokie, Ill.

recrystallized from toluene; however, it was necessary in the case of the higher molecular weight compounds to use pyridine. The oxazoles and oxadiazoles were recrystallized from hexane, toluene or pyridine, depending on the complexity of the sub-

stituents. For use as a scintillation solute, extreme purity is required. A method often found advantageous was to filter the hot recrystallization mixture, after addition of decolorizing carbon, through a short column of activated alumina.

TABLE III



| Ar ₁ | Ar ₂ | X | Formula | M.p., ^a °C. | Nitrogen, % Calcd. | Found |
|---|---|----------------------------|---|---------------------------|-----------------------|-------|
| C ₆ H ₅ | C ₆ H ₅ | Perchlorate | C ₁₆ H ₁₄ ClNO ₅ | 177-188 | 4.17 | 4.20 |
| C ₆ H ₅ | C ₆ H ₅ | <i>p</i> -Toluenesulfonate | C ₂₃ H ₂₁ NO ₄ S | 170-172 | 3.44 | 3.25 |
| 4-C ₆ H ₅ C ₆ H ₄ | 4-C ₆ H ₅ C ₆ H ₄ | <i>p</i> -Toluenesulfonate | C ₃₅ H ₂₉ NO ₄ S | 214-216 | 2.50 | 2.52 |
| C ₆ H ₅ | 1-C ₁₀ H ₇ | <i>p</i> -Toluenesulfonate | C ₂₇ H ₂₃ NO ₄ S | 144-145 | 3.06 | 2.91 |

^a Melting points taken on a Fisher-Johns melting point block. Microanalyses by Micro-Tech Laboratories, Skokie, Ill.

Experimental Part

The following procedures are illustrative of the methods used.

N,N'-Diphenacylterephthalamide.—To a stirred solution of 25.0 g. (0.123 mole) of terephthalyl chloride in 300 ml. of dry pyridine, was slowly added 43.0 g. (0.25 mole) of phenacylammonium chloride. The mixture was refluxed for 15 minutes, then allowed to cool and diluted with water. The crude product was filtered, dried and recrystallized from *ca.* 2 l. of pyridine; the yield was 28.5 g. (58%).

1,4-Di-[2-(5-phenyloxazolyl)]-benzene (POPOP).—A mixture of 13.5 g. (0.034 mole) of N,N'-diphenacylterephthalamide in 500 ml. of phosphorus oxychloride was refluxed overnight. Most of the phosphorus oxychloride was distilled from the reaction mixture, and the residue was slowly added to water contained in a 3-l. beaker. The solid was filtered, washed with water, dried and recrystallized from pyridine; the yield was 10.3 g. (84%).

1-Benzoyl-2-(4-phenylbenzoyl)-hydrazine.—Ten grams (0.074 mole) of benzoylhydrazine was added to a stirred solution of 16 g. (0.074 mole) of *p*-phenylbenzoyl chloride

in 100 ml. of dry pyridine. The mixture was refluxed for 20 minutes, cooled and treated with water to completely precipitate the crude product. This material was filtered, dried and recrystallized from toluene; the yield was 13.3 g. (57.7%, m.p. 222-224°).

2-Phenyl-5-(4-biphenyl)-1,3,4-oxadiazole (PBD).—Seventy-six grams (0.24 mole) of 1-benzoyl-2-(4-phenylbenzoyl)-hydrazine in 200 ml. of phosphorus oxychloride was gently refluxed overnight. Most of the phosphorus oxychloride was distilled from the reaction mixture, and the residue was slowly added to water. The oxadiazole was filtered, washed with water, dried and recrystallized from toluene; the yield was 52.0 g. (73%).

2,5-Di-(4-biphenyl)-3-methyloxazolium *p*-Toluenesulfonate (MBBO).—A mixture of 3.7 g. (0.02 mole) of methyl *p*-toluenesulfonate and 3.7 g. (0.01 mole) of 2,5-di-(4-biphenyl)-oxazole was heated in an oil-bath at 100° for 1.5 days. The viscous liquid was cooled and dissolved in a small amount of methanol. The addition of dry ether and cooling gave 7.3 g. (99%) of white, crystalline product.

LOS ALAMOS, N. M.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

γ -Pyridones by Isomerization. Substituted 1-Methyl-3,5-dibenzyl-4-pyridones

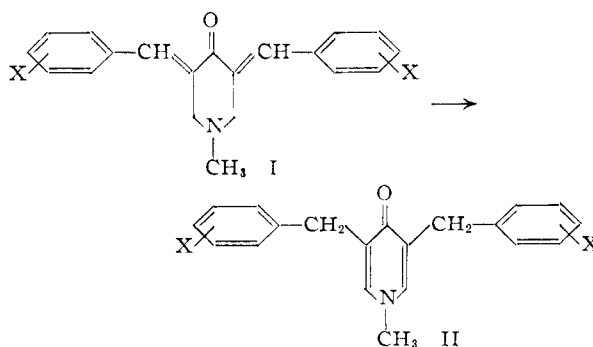
BY NELSON J. LEONARD AND DAVID M. LOCKE^{1,2}

RECEIVED SEPTEMBER 20, 1954

The isomerization of substituted 1-methyl-3,5-dibenzylidene-4-piperidones to the correspondingly substituted 1-methyl-3,5-dibenzyl-4-pyridones has been effected in boiling ethylene glycol solution using palladium-on-charcoal. The general method extends the range of this type of aromatization reaction to heterocyclic compounds and marks the introduction of ethylene glycol as a useful solvent for this conversion.

The efficacy of the aromatization reaction in converting 2,6-dibenzylidenecyclohexanone to 2,6-dibenzylphenol³⁻⁵ and substituted 3,7-dibenzylidene-1,2-cycloheptanediones to the correspondingly substituted 3,7-dibenzyltropolones^{6,4} suggested that this reaction might be of equal value in the analogous heterocyclic systems. Accordingly, we have studied, as a first example of heterocyclic aromatizations of this type, the isomerization of a series of substituted 1-methyl-3,5-dibenzylidene-4-piperidones (I) to the corresponding 1-methyl-3,5-dibenzyl-4-pyridones (II).

We were encouraged in our belief that the isomerization of I to II would in general occur readily because of the aromatic character—and hence



| | | | | | |
|---|---------------------------|---|-----------------------------|---|--|
| a | H | e | <i>m</i> -NO ₂ | i | <i>p</i> - <i>i</i> -C ₃ H ₇ |
| b | <i>p</i> -CH ₃ | f | <i>p</i> -Cl | j | <i>p</i> -(CH ₃) ₂ N |
| c | <i>o</i> -CH ₃ | g | <i>o</i> -Cl | k | <i>p</i> -C ₆ H ₅ |
| d | <i>p</i> -NO ₂ | h | <i>p</i> -CH ₃ O | | |

comparatively greater stability—of the 4-pyridone nucleus, as suggested by Arndt⁷ and amply con-

(7) (a) F. Arndt and A. Kalischek, *Ber.*, **63**, 587 (1930); (b) F. Arndt, *ibid.*, **63**, 2963 (1930); (c) F. Arndt, P. Nachtwey and J. Pusch, *ibid.*, **58**, 1633 (1925).

(1) Sinclair Refining Company Fellow in Organic Chemistry, 1952-1953. Work done under the sponsorship of the Sinclair Research Laboratories, Inc.

(2) National Science Foundation Fellow, 1953-1954.

(3) R. Weiss and J. Ebert, *Monatsh.*, **65**, 399 (1935).

(4) N. J. Leonard and G. C. Robinson, *THIS JOURNAL*, **75**, 2143 (1953).

(5) E. C. Horning, *J. Org. Chem.*, **10**, 263 (1945).

(6) N. J. Leonard and J. W. Berry, *THIS JOURNAL*, **75**, 4989 (1953).