

lization from absolute ethanol melted at 130–131° (lit.¹³ mp 130–131°). The infrared spectrum exhibits sharp absorption bands at 1445, 1385, 970, 775, 765, 745, and 720 cm⁻¹. The ultraviolet spectrum is characterized by absorption at $\lambda_{\text{max}}^{\text{EtOH}}$ 227 m μ (ϵ 30,300), 234 (29,500), and 255 (15,700). The nmr spectrum (CCl₄) exhibits signals at τ 2.6–3.1 (multiplet), 3.50 (singlet), and 6.55 (singlet) in the respective area ratio of 4:1:2. A mixture melting point determination with an authentic sample¹³ showed no depression, and the infrared spectrum was identical with that of authentic material.

Anal. Calcd for C₁₈H₁₄: C, 93.87; H, 6.13. Found: C, 93.58; H, 6.18.

Evaporation of the later chromatographic fractions afforded 330 mg (14.5%) of an orange, crystalline solid which was recrystallized from absolute ethanol but still melted over a wide range. Further purification of this material was achieved by chromatography through a 30-cm chromatographic column packed with acid-washed aluminum oxide. The central part of the bright orange band was collected and after removal of the volatile solvent, 45 mg of pure *sym*-dibenzfulvalene (Ia) remained. The golden orange leaflets of Ia upon heating begin to darken at 220° but do not melt up to 300°. The infrared spectrum of this material exhibits significant bands at 1445, 1370, 780, and 740 cm⁻¹. The ultraviolet spectrum is characterized by absorption at $\lambda_{\text{max}}^{\text{hexane}}$ 248 m μ (ϵ 19,300), 285 (22,300), 291 (shoulder) (20,900), 360 (shoulder) (18,300), 380 (27,200), and 401 (30,000). See Figure 1 for a comparison with Ib. The nmr spectrum (CCl₄) shows absorption at τ 2.0–2.3 (multiplet) and 2.5–3.1 (multiplet) in the respective ratio of 1:5.

Anal. Calcd for C₁₈H₁₂: C, 94.70; H, 5.30. Found: C, 94.86; H, 5.21.

Treatment of Vb with 2 Equiv of Potassium Amide in Liquid Ammonia.—By a procedure analogous to that above, the dibromide, Vb (2.5 g, 6.4 mmoles), on treatment with potassium amide generated from potassium metal (0.5 g, 0.125 g-atom), iron powder (1.0 g), and anhydrous liquid ammonia (50 ml), provided 100 mg (7%) of Ia. No traces of 3,3'-biindenyl (VII) could be detected.

Treatment of the Diiodide Vc with Potassium *t*-Butoxide.—To a solution of potassium *t*-butoxide, prepared from potassium metal (0.750 g, 0.019 g-atom) in 50 ml of dry *t*-butyl alcohol (distilled from sodium metal), was added the diiodide (1.5 g, 3.1 mmoles). The resulting mixture was stirred at 75° for 6 hr. After cooling to room temperature, the volatile solvents were removed under reduced pressure (rotary evaporator) and the residue was suspended in water (50 ml) and extracted with two 100-ml portions of ether. The ether extracts were combined and washed in turn with 5% hydrochloric acid (100 ml), 5% sodium thiosulfate solution (100 ml), and finally water (200 ml). After drying over sodium sulfate the ether solution was evaporated and the dark brownish orange residue was dissolved in the minimum amount of benzene. The benzene solution was then applied on a 30-cm column packed with neutral aluminum oxide. Elution was begun with 1:4 benzene-cyclohexane (100 ml) and continued with 1:3 benzene-cyclohexane (100 ml), 1:1 benzene-cyclohexane (200 ml), and pure benzene (200 ml). Evaporation of the first 100 ml of yellow-orange eluate afforded a total of 8 mg (1%) of the dibenzfulvalene (Ia) as an orange, crystalline solid. Later eluates afforded only dark, intractable oils.

Treatment of 3,3'-Biindenyl (VII) with Tetrachloro-1,2-benzoquinone.—A solution of VII (70 mg, 0.3 mmole) and tetrachloro-1,2-benzoquinone (*o*-chloranil, 75 mg, 0.3 mmole) in 25 ml of dry benzene (distilled from sodium metal) was maintained at reflux for 20 hr. The light orange solution was subsequently evaporated to dryness, the residue was dissolved in the minimum amount of 1:1 benzene-hexane, and the resultant solution was applied on a 30-cm chromatographic column, packed with acid-washed aluminum oxide, and eluted with 1:5 benzene-hexane. Evaporation of the initial colorless eluate afforded 40 mg (57%) of unreacted diene VII. Evaporation of the yellow eluate that followed yielded a dark orange oil (25 mg) which could not be induced to crystallize. The ultraviolet spectrum of this material exhibited absorption at $\lambda_{\text{max}}^{\text{hexane}}$ 380 and 401 m μ , which is characteristic of the dibenzfulvalene.

Catalytic Hydrogenation of 3,3'-Biindenyl (VII) and of *sym*-Dibenzfulvalene (Ia).—3,3'-Biindenyl (30 mg, 0.13 mmole), heptane (60 ml), and 5% palladium on charcoal (50 mg) were placed in a hydrogenation flask and the pressure was raised to 50 psi of hydrogen at room temperature. The mixture was shaken for 24 hr. Removal of the catalyst by filtration afforded a colorless

heptane solution which exhibited ultraviolet absorption at λ_{max} 260.5, 267, and 273.5 m μ . *sym*-Dibenzfulvalene was hydrogenated as described above, and under a pressure of 63 psi of hydrogen. The ultraviolet spectrum of the resultant colorless heptane solution was qualitatively identical with that of the product obtained by reduction of 3,3'-biindenyl. After removal of most of the heptane under reduced pressure, the residual materials from the two hydrogenations exhibited identical infrared spectra (CCl₄).

Acknowledgment.—We are indebted to the National Science Foundation (Grants G-13759, G.P. 3764, and G.P. 2543) for financial support of this work. We also gratefully acknowledge Mr. Gary Gaffney for technical assistance.

The Oxidation of Some Benzhydrols with Bromine in Methanol^{1a}

K. G. RUTHERFORD AND O. A. MAMER^{1b}

The Department of Chemistry, University of Windsor,
Windsor, Ontario, Canada

Received December 15, 1966

A recent discovery in our laboratory of a novel synthesis of mixed ethers from the reaction of some arylcarbinols with simple aliphatic alcohols in the presence of iodine,² has prompted an investigation into the limitations of the reaction. It was found that benzhydrols which were substituted in the 4 position by electron-seeking groups gave reduced yields of mixed ethers and in the case of 4-nitrobenzhydrol no reaction was observed. The same carbinol, however, when treated with bromine in methanol was converted to 4-nitrobenzophenone in nearly quantitative yield. Table I indicates the results obtained from this very simple oxidation procedure with other benzhydrols as well as with benzyl alcohol, 4-nitrobenzyl alcohol, triphenylcarbinol, and phenyl-*p*-tolyl- α -naphthylcarbinol.

TABLE I

Alcohol ^a	Product	% yield
(R) ₂ CHOH	Benzophenone	45%
RR ₁ CHOH	4-Chlorobenzophenone	Ca. quant
RR ₂ CHOH	4-Bromobenzophenone	Ca. quant
R ₁ R ₂ CHOH	4-Chloro-4'-bromobenzophenone	Ca. quant
RR ₃ CHOH	4-Nitrobenzophenone	Ca. quant
R ₂ R ₃ CHOH	4-Bromo-4'-nitrobenzophenone	Ca. quant
RR ₄ CHOH	4-Methylbenzophenone	81%
R ₃ R ₅ CHOH	4-Nitro-4'- <i>t</i> -butylbenzophenone	95%
RCH ₂ OH	Benzaldehyde	20%
R ₂ CH ₂ OH	4-Bromobenzaldehyde	40%
R ₃ CH ₂ OH	4-Nitrobenzaldehyde	80%
(R) ₃ COH	Methyl ether	Ca. quant
RR ₄ R ₆ COH	Methyl ether	80%

^a R = C₆H₅; R₁ = 4-ClC₆H₄; R₂ = 4-BrC₆H₄; R₃ = 4-NO₂-C₆H₄; R₄ = 4-CH₃C₆H₄; R₅ = 4-*t*-BuC₆H₄; R₆ = α -naphthyl.

As can be seen from the table, the yields of oxidation product are excellent in all cases where the algebraic sums of the Hammett σ values of the ring substituents

(1) (a) This research was supported in part by a grant from the Petroleum Research Fund of the American Chemical Society and in part by the Ontario Research Foundation. Grateful acknowledgement is hereby rendered to both granting agencies. (b) Holder of a National Research Council of Canada Studentship.

(2) K. G. Rutherford and O. A. Mamer, submitted for publication.

(including hydrogen) have a positive value. It is rather surprising that 4-methylbenzhydrol gave a better yield of ketone than did benzhydrol. Interestingly, Arnett³ found that both of these compounds gave a nearly quantitative yield of corresponding ketone when treated with a solution of bromine in acetic acid to which sodium bromide had been added.³ The effect of the nitro group can be seen by the difference in reactivity of benzyl alcohol *vs.* 4-nitrobenzyl alcohol which gave a much better yield of corresponding aldehyde. Triphenylcarbinol as well as phenyl-*p*-tolyl- α -naphthylcarbinol gave excellent yields of corresponding methyl ethers as expected.

Experimental Section

All melting points are uncorrected. Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

All of the benzhydrols (except diphenylcarbinol which was obtained from commercial sources) were prepared from reduction of the corresponding benzophenones. Lithium aluminum hydride was used as the reducing agent in all cases with the exception of benzophenones which were substituted with the nitro group. Sodium borohydride was used in these latter cases and the nitro group remained unaffected with this reagent.

The substituted benzophenones were prepared in good yields with the use of the Friedel-Crafts reaction of appropriate acyl halide and benzenoid moiety. With the exception of 4-nitro-4'-*t*-butylbenzophenone, 4-nitro-4'-bromobenzhydrol, and 4-nitro-4'-*t*-butylbenzophenone, all ketones and alcohols are well characterized in the literature. Phenyl-*p*-tolyl- α -naphthylcarbinol was prepared according to the method of Schlenk and Meyer.⁴ Benzyl alcohol and 4-nitrobenzyl alcohol were obtained from commercial sources.

Bromine Oxidations.—The benzhydrols were dissolved in a liberal amount of absolute methanol. Bromine (0.5 *M* excess) was added to the cold solution. The mixture was allowed to stir at room temperature overnight although it was found that in the case of nitro-substituted benzhydrols, the oxidation was complete in approximately 2 hr. The mixture was poured into ice-water which contained sodium thiosulfate to destroy any unreacted bromine. The ketonic fragment usually crystallized without difficulty and was recovered by filtration. Benzaldehyde was recovered by distillation. The oxidation of 4-nitrobenzhydrol and 4-nitrobenzyl alcohol is described below as illustrative of the procedure.

Ether Formation.—The procedure described above for oxidation was followed. The triaryl-substituted carbinols, however, were converted to corresponding methyl ethers. Only a catalytic amount of bromine was needed for this conversion although the reaction proceeded best when approximately equimolar amounts of bromine were used. The methyl ether of triphenylcarbinol has previously been characterized. A mixture melting point determination of the methyl ether prepared by the above described method and by the reaction of triphenylmethyl chloride and methanol in the presence of pyridine was not depressed. The methyl ether of phenyl-*p*-tolyl- α -naphthylcarbinol has been recorded by Dilthey⁵ as melting at 120–121°. We found the ether to melt at 50–52°. The infrared spectrum showed aromatic skeletal vibrations at 1605 and 1495 cm^{-1} and C=O stretching at 1076 and 1072 cm^{-1} . No OH stretching band was observed.

Anal. Calcd: C, 88.73; H, 6.54. Found: C, 88.70; H, 6.61.

4-Nitro-4'-*t*-butylbenzophenone.—*t*-Butylbenzene (150 g, 1.1 moles), 4-nitrobenzoyl chloride (230 g, 1.25 moles), and aluminum chloride (200 g, 1.5 moles) were placed in a 2-l. resin kettle. After 3 hr of stirring at room temperature, the reaction mixture, which had set to a black solid was chipped from the kettle and hydrolyzed in ice-water. The resultant solid was isolated by filtration and air dried. Recrystallization from a chloroform-

petroleum ether (bp 30–60°) solvent pair yielded 125 g (40%) of pure ketone, mp 112–113°. Strong bands appeared in the infrared spectrum at 1670, 1530, 1360, and 850 cm^{-1} indicating C=O stretching, NO₂ asymmetric and symmetric stretching, and CN stretching.

Anal. Calcd: C, 72.2; H, 6.05. Found: C, 72.6; H, 6.13.

4-Nitro-4'-*t*-butylbenzhydrol.—A solution of 94 g (0.33 mole) of 4-nitro-4'-*t*-butylbenzophenone and 500 ml tetrahydrofuran was cooled to ice-bath temperature and stirred mechanically. To this solution was added 5 g (0.132 mole) of sodium borohydride in 0.5-g portions each dissolved in 2 ml of ice-water. The rate of addition was adjusted to maintain the temperature of the mixture below 15°. After an additional 15-min period of stirring, the dark green solution was poured slowly with stirring on a mixture of cracked ice and hydrochloric acid. The mixture was stirred overnight under a current of air. A yellow precipitate was obtained which was recovered by filtration and weighed (93 g, 99% crude). The product was recrystallized from an acetone-water solvent pair (mp 110–111°). A weak band at 3580 and strong bands at 1525 and 1350 cm^{-1} in the infrared spectrum appeared indicating OH stretching and asymmetric and symmetric NO₂ stretching, respectively.

Anal. Calcd: C, 71.7; H, 6.72. Found: C, 72.3; H, 6.91.

4-Nitro-4'-bromobenzhydrol.—This compound was prepared according to the above procedure. 4-Nitro-4'-bromobenzophenone (260 g, 0.85 mole) was reduced with 12 g (0.315 mole) of sodium borohydride to yield 255 g (92%) of product, mp 160–161°. A weak band at 3580 and strong bands at 1525 and 1352 cm^{-1} appeared in the infrared spectrum indicating OH stretching and asymmetric and symmetric NO₂ stretching, respectively.

Anal. Calcd: C, 50.7; H, 3.28; Br, 25.9. Found: C, 50.9; H, 3.38; Br, 26.1.

4-Nitrobenzophenone.—A solution of 5 g (0.0219 mole) 4-nitrobenzhydrol, 15 g (0.094 mole) bromine, and 50 ml of absolute methanol was stirred at room temperature for 2 hr. The reaction mixture was poured slowly into an ice-cold solution of sodium thiosulfate. Elementary sulfur was liberated as well as an oil that crystallized on standing (mp 134–136°). The yield was 5.0 g (100%). A mixture melting point determination with an authentic sample was not depressed.

4-Nitrobenzaldehyde.—In a manner similar to that described above a yield of 8.1 g (80%), mp 105–106°, of 4-nitrobenzaldehyde was obtained from the reaction of 10 g (0.064 mole) of 4-nitrobenzyl alcohol and 0.15 g (0.094 mole) of bromine in 100 ml of absolute methanol.

A New Synthesis of 2-Pyridine Aldoximes

FRANCIS A. DANIHER,¹ BRENNIE E. HACKLEY, JR.,²
AND ARTHUR B. ASH¹

Ash Stevens Inc., Detroit, Michigan, and
Research Laboratories, U. S. Army Edgewood Arsenal,
Edgewood Arsenal, Maryland

Received March 28, 1966

The use of 2-pyridine aldoxime methiodide (2-PAM) as an antidote for organophosphorus poisons has stimulated interest to find new convenient routes for the synthesis of the precursor 2-pyridine aldoximes.³

The classical method for the syntheses of these compounds involves acetic anhydride rearrangement⁴ of the corresponding 2-picoline N-oxide to the acetate of 2-pyridinemethanol, hydrolysis of the acetate to the alcohol, oxidation of the carbinol to the aldehyde, and then conversion of the aldehyde to the oxime. The over-all yield for this multistep sequence for a series of

(1) Ash Stevens, Inc.

(2) U. S. Army Edgewood Arsenal.

(3) See D. F. Heath, "Organophosphorus Poisons," Pergamon Press Inc., New York, N. Y., 1961.

(4) V. Boeckleheide and W. Linn, *J. Am. Chem. Soc.*, **76**, 1286 (1954); V. J. Traynelis and P. L. Pacini, *ibid.*, **86**, 4917 (1964).

(3) E. M. Arnett and G. B. Klingensmith, *J. Am. Chem. Soc.*, **87**, 1023 (1965). Indeed E. M. A. suggested that less activated benzhydrols would undergo oxidation rather than cleavage with bromine. Benzhydrols which were substituted by methoxy groups were cleaved by the action of bromine in aqueous acetic acid.

(4) W. Schlenk and E. Meyer, *Ber.*, **52B**, 17 (1919).

(5) W. Dilthey, E. Haussler, E. Hausdorfer, and O. Reek, *J. Prakt. Chem.*, **109**, 313 (1925).