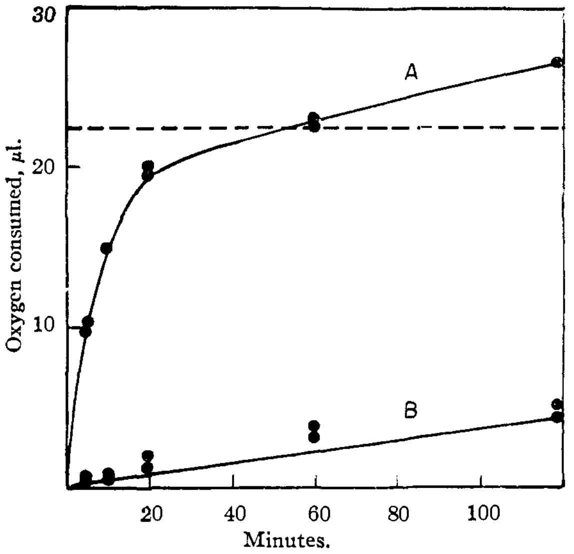

Fig. 1.—Oxygen consumption by coniferyl alcohol in the presence of mushroom extracts. Each Warburg vessel contained 4 µmoles of coniferyl alcohol dissolved in 2.8 ml. of 0.1 *M* phosphate buffer, *p*H 6.8, in addition to, (A) 4 mg. of Freudenberg oxidase (160 catecholase units), (B) 4 mg. of Freudenberg oxidase heated to 100° for 3 minutes, or 160 catecholase units of purified mushroom polyphenoloxidase, or 3 µmoles of cupric ion. The dotted line indicates an amount of oxygen equivalent to $^1/_2$ atom per molecule of coniferyl alcohol. KOH was present in the central well.

tion in accord with the earlier work. However, in the presence of the same number of catecholase units[14] of purified mushroom polyphenoloxidase[15] the oxygen consumption was negligible, as was the case in the presence of boiled Freudenberg oxidase, or cupric ion.

We conclude that there is present in crude mushroom extracts a heat-labile system which catalyzes the consumption of some oxygen by coniferyl alcohol, but it is not polyphenoloxidase which does this. The present experiments do not rule out a biosynthetic relationship between the lignins and melanins but they do show that the particular process proposed by Freudenberg is not pertinent to the concept.

Experimental

Coniferyl Alcohol.—The coniferyl alcohol was prepared by the lithium aluminum hydride reduction of ethyl acetoferulate using a modification of the method of Allen and Byers.[16] The ester (0.025 mole) was added in one portion to a solution of lithium aluminum hydride (0.100 mole) in 800 ml. of ether at −60°. The temperature was allowed to rise to 0° over a period of 1.5 hours and the solution was then filtered and the salt was hydrolysed and crystallized as described.[16] This method gave a product which crystallized immediately and without difficulty from the petroleum ether–ether mixture.

DEPARTMENT OF BIOCHEMISTRY
UNIVERSITY OF OREGON MEDICAL SCHOOL
AND THE DEPARTMENT OF CHEMISTRY
REED COLLEGE
PORTLAND, OREGON

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[14] W. H. Miller, M. F. Mallette, L. J. Roth and C. R. Dawson, THIS JOURNAL, **66**, 514 (1944).

[15] The Treemond Company, New York, supplied our preparation, which contained 6200 catecholase units per ml., or 1510 units per mg.

[16] C. F. H. Allen and J. R. Byers, Jr., THIS JOURNAL, **71**, 2683 (1949).

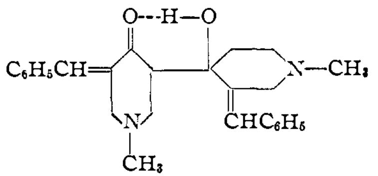
Piperidine Derivatives. XXVI. 1-Methyl-3-benzal-4-piperidone Dimer

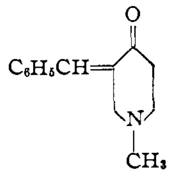
BY S. M. MCELVAIN AND P. HAROLD PARKER, JR.[1]

RECEIVED AUGUST 18, 1954

The dimeric structure I is now assigned to the compound described as 1-methyl-3-benzal-4-piperidone (II) in paper XVIII of this series.[2] This compound was obtained in the earlier work from 1-methyl-4-piperidone and benzaldehyde as well as from 1-methyl-3,5-dibenzal-4-piperidone (III) when the reaction was carried out in a solvent (4% solution of potassium hydroxide in 60% ethanol) from which III did not precipitate. The structure II was assigned on the basis of the elemental analyses and the methods by which it had been prepared, although some concern was expressed over the much lower solubility of the monobenzal derivative II as compared to that of the dibenzal derivative III; also the melting point of the former compound (224°) is considerably higher than that of the latter (117°).[3]

In the present work doubt was cast on the structure II when it was found that (a) the compound could not be converted to the dibenzal derivative III, although the reverse transformation is possible[2] and (b) the hydrogenation of the compound did not yield the expected 1-methyl-3-benzyl-4-piperidone,[4] but a compound with a wide melting range (85–95°) that showed a molecular weight of *ca.* 390. The structure I accounts for these results as well as for the following observations: the compound (a) shows a molecular weight of 408 (calcd. for I, 402), (b) has a broad associated hydroxyl band joining the C–H band at 3.3 µ and also a hydrogen bonded, conjugated carbonyl band at 6.1 µ in the infrared spectrum,[5] (c) shows a maximum absorption at 290 mµ (log ε 4.43) in the ultraviolet spectrum[6] and (d) yields an acetate in whose infrared spectrum there is no hydroxy band and in which the α,β-unsaturated carbonyl band, which is apparent in the ultraviolet spectrum, is masked by the ester carbonyl band at 5.75 µ.


I


II

It is possible that the high melting point of I and its insolubility in non-polar solvents may be due to a salt-like character resulting from the interaction of the carbonyl group which is posi-

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[1] Wisconsin Alumni Research Foundation Research Assistant (1953).

[2] S. M. McElvain and K. Rorig, THIS JOURNAL, **70**, 1820 (1948).

[3] It may also be noted that the analog of II, 2-benzalcyclohexanone, is reported, (D. Vorländer and K. Kunze, *Ber.*, **59**, 2078 (1926), to melt at 54° and can be converted quantitatively to 2,6-dibenzalcyclohexanone, m.p. 118°.

[4] This compound, a liquid, b.p. 104–105° (0.1 mm.), has been prepared in this Laboratory by Martin D. Barnett by the decarbethoxylation of 1-methyl-3-benzyl-3-carbethoxy-4-piperidone, which was obtained by the benzylation of 1-methyl-3-carbethoxy-4-piperidone.

[5] *Cf.* R. S. Rasmussen, D. D. Tunnicliff and R. R. Brattain, THIS JOURNAL, **71**, 1068 (1949).

[6] *Cf.* L. Dorfman, *Chem. Revs.*, **53**, 47 (1953)

tively polarized by hydrogen bonding with the basic nitrogen of another ring.[7]

Experimental[8]

Dimer of 1-Methyl-3-benzal-4-piperidone (I).—The following improved method was used for this product. To 1.13 g. of 1-methyl-4-piperidone and 1.06 g. of benzaldehyde in 2 ml. of 95% ethanol was added 0.3 g. of potassium hydroxide in 1 ml. of water. The solution was stirred and heated at 60–70° for four hours. The precipitate was filtered and triturated with water. When dried the light yellow solid weighed 1.47 g. (73%), m.p. 193–207°. Recrystallization from 95% ethanol afforded an analytical sample, m.p. 224–225°. The product I showed a strong tendency to form supersaturated solutions in ethanol, but recrystallization could be achieved by dissolution in a minimum of hot ethanol followed by distillation of about two-thirds of the ethanol. This product had the same analyses and its melting point was not depressed by a sample prepared in the earlier work;[2] mol. wt. (Rast) 408.

Hydrogenation of I.—To 2.01 g. of I was added 11.9 ml. of 0.839 *N* hydrochloric acid and 0.15 g. of Adams platinum oxide catalyst. The solution was shaken with hydrogen at 38 pounds pressure until two equivalents of hydrogen per mole of I had been absorbed (65 minutes). The solution was filtered to remove the catalyst and neutralized with sodium hydroxide to give a white solid with wide melting range (85–95°), which could not be narrowed by recrystallization; mol. wt. (Rast) 390.

Acetate of I.—To a mixture of 2.01 g. of I and 0.75 g. of fused sodium acetate under nitrogen were added 10 ml. of acetic anhydride. The mixture was heated at 110° with stirring for two hours, cooled and poured into 75 ml. of ice-water. After standing for one hour the aqueous solution was neutralized with sodium bicarbonate. The resulting fluffy, white precipitate was washed with water, dried, dissolved in ether and filtered. The ether solution was poured onto a 38-cm. column of Alcoa activated alumina F-20. Elution of ether–isopropyl alcohol solution (100–0.25) gave 1.3 g. of solid which was triturated with isopropyl ether and recrystallized from ethyl ether to give an analytical sample of the acetate of I; m.p. 170–172°.

Anal. Calcd. for $C_{28}H_{32}N_2O_3$: C, 75.64; H, 7.26. Found: C, 75.38; H, 7.10.

This acetate of I had an ultraviolet absorption maximum at 287 mμ (log ε 4.43) and molecular weight (Rast) 455. Further elution of the column with ether–isopropyl alcohol (10:1) gave 0.5 g. of an oil that failed to crystallize.

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(7) For examples of interaction between a nitrogen and a carbonyl group see N. J. Leonard, R. C. Fox, M. Oki and S. Chiavarelli, THIS JOURNAL, **76**, 630 (1954).

(8) Spectra were determined with a Cary Ultraviolet Recording Spectrophotometer, model 11MS and a Baird Double Beam Infrared Recording Spectrometer, model B, fitted with a sodium chloride prism. Ultraviolet adsorption spectra were determined in ethanol. Infrared adsorption spectra were determined in a Nujol mull.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON 6, WISCONSIN

Some Reactions with Chlorendic Anhydride[1]

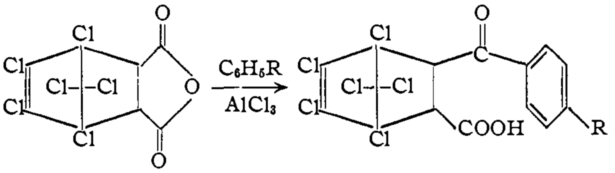
BY E. T. MCBEE AND W. R. DIVELEY[2]

RECEIVED JULY 21, 1954

In connection with other investigations in this Laboratory concerning hexachlorocyclopentadiene and its derivatives,[3–5] chlorendic anhydride was examined with respect to its behavior in the Friedel–Crafts reaction and toward aqueous ammonia.

If chlorendic anhydride is regarded as a substituted succinic anhydride, it can be expected to act as an acylating agent in the Friedel–Crafts reaction.[6] Its non-chlorinated analog, bicyclo-[2.2.1]5-heptene-2,3-dicarboxylic anhydride, however, does not react with benzene and aluminum chloride, whereas the corresponding saturated compound does.[7]

It has now been established that chlorendic anhydride reacts with benzene and toluene in the presence of aluminum chloride to give the expected keto acids in yields of 85–89%.



I II

The acids II (R = H, Me) can be esterified but fail to cyclize on heating with concentrated or fuming sulfuric acid, which was also observed in the case of the analogous 3-benzyl-norcamphane-2-carboxylic acid.[7]

The crystalline imide of chlorendic acid may be prepared in excellent yield by the reaction of chlorendic anhydride with aqueous ammonia at room temperature.

Experimental[8]

Chlorendic Anhydride.—Commercial chlorendic anhydride[9] was purified by refluxing with acetyl chloride for 2 hours immediately before use. After cooling the mixture was filtered with suction, washed twice with anhydrous ether and warmed briefly on a steam-bath to remove residual ether.

3-Benzoyl-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]5-heptene-2-carboxylic Acid.—Chlorendic anhydride (37.1 g., 0.1 mole) was dissolved in 150 ml. of dry, thiophene-free benzene. To this solution was added all at once 38.5 g. (0.29 mole) of pulverized aluminum chloride. An immediate exothermic reaction was controlled by cooling. After the reaction had subsided, the mixture was refluxed gently for one hour. After cooling, the mixture was hydrolyzed by cautious addition, with stirring, of 50 ml. of water, followed by 100 ml. of 10% hydrochloric acid. The mixture was allowed to stand overnight and steam distilled to remove the benzene. The solid, which remained in the residue, was filtered with suction and digested with two 400-ml. portions of boiling water. The remaining tan solid was decolorized with Norit and crystallized from benzene. Drying of the crude, m.p. 187–192°, at 130° and recrystallizing from the same solvent gave colorless prisms, m.p. 196–197°, yield 85%.

Anal. Calcd. for $C_{15}H_8O_3Cl_6$: C, 40.09; H, 1.78; neut. equiv., 449. Found: C, 40.12; H, 2.07; neut. equiv., 446.

Ethyl Ester.—On esterification with ethanol and sulfuric acid, the acid was converted to the ethyl ester, m.p. 80–81°.

Anal. Calcd. for $C_{17}H_{12}Cl_6O_3$: C, 42.80; H, 2.53. Found: C, 42.74; H, 2.21.

1,4,5,6,7,7-Hexachloro-3-(*p*-toluyl)-bicyclo[2.2.1]5-heptene-2-carboxylic Acid.—The analogous reaction of 37.1 g. (0.1 mole) of chlorendic anhydride, 150 ml. of toluene and

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(1) The simple name "chlorendic anhydride" for 1,4,5,6,7,7-hexachlorobicyclo[2.2.1]5-heptene-2,3-dicarboxylic anhydride conforms to the International system of nomenclature and to the system of Patterson and Capell in the "Ring Index" (*Chem. Eng. News*, **32**, 873 (1954)).

(2) Abstracted from the doctoral thesis of W. R. Diveley, Purdue University, 1952.

(3) E. T. McBee and C. F. Baranauckas, *Ind. Eng. Chem.*, **41**, 806 (1949).

(4) J. S. Newcomer and E. T. McBee, THIS JOURNAL, **71**, 946, 952 (1949).

(5) E. T. McBee, H. Rakoff and R. K. Meyers, *ibid.*, **77**, in press.

(6) R. Adams, "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 229.

(7) M. S. Morgan, R. S. Tipson, A. Lowy and W. E. Baldwin, THIS JOURNAL, **66**, 404 (1944).

(8) All temperatures are uncorrected.

(9) The authors are indebted to the Hooker Electrochemical Company for a generous supply of this anhydride.