hydrogenation flask and the flask was reconnected to the hydrogenator. Propyl alcohol was obtained quantitatively in less than 0.5 hr from each experiment with cinnamic acid and the butylene oxides. Also, the epoxides were not rearranged to carbonyl compounds by the catalyst.

The catalyst is exceedingly simple to prepare and use. It may be prepared in the hydrogenation flask directly or in larger quantities in a centrifuge flask. The catalyst may be isolated by centrifuging the flask, stored indefinitely under nitrogen, either dry or under ethanol, and used as needed.

The results indicate that nickel boride has a great utility in the syntheses of complex organic compounds, not just for the reduction of olefins or acetylenes. While other materials have been reported[6] capable of catalyzing these conversions, nickel boride has not been found to catalyze rearrangements, hydrogenolyses, or carbonyl reductions which can accompany catalytic hydrogenations. We are currently studying the hydrogenation of nitrogen-containing compounds and the use of aprotic solvents to extend the applications of nickel boride.

Experimental Section

Chemicals.—2-Butene-1,4-diol and 2-butyne-1,4-diol were supplied by Antara Chemical Co. 2-Cyclopentene-1,4-diol was prepared by the method of Owen and Smith.[7] 1-Phenyl-2-propenol was prepared by the method of Braude, *et al.*[8] Maleic acid was prepared from the anhydride by the method of Vogel.[9] Cinnamaldehyde was extracted with dilute sodium bicarbonate solution to remove any acid present. Cinnamic acid was converted to the sodium salt which was dissolved in water and extracted with benzene, chloroform, and ether. Addition of gaseous hydrogen chloride precipitated cinnamic acid from the aqueous solution. All other compounds were used from the bottles with no purification.

Catalyst Preparation.—For a single hydrogenation, 1.24 g (5 mmol) of powdered nickel acetate, 50 ml of 95% ethanol, and a short spinbar are placed in the hydrogenation flask. Stirring is begun and the flask flushed with hydrogen. Injection of 5 ml of 1.0 *M* sodium borohydride into the flask produces the black colloidal catalyst.

For the bulk catalyst, the above procedure is followed using larger amounts of nickel acetate and sodium borohydride solutions and a large centrifuge tube. The colloidal catalyst is easily separated from the solution by centrifuging at 3000 rpm for several minutes. The isolated catalyst can be stored under nitrogen indefinitely, either dry or under ethanol.

Hydrogenation Procedure.—To the catalyst and preparatory solutions in the hydrogenation flask is added 10 mmol of the compound to be hydrogenated, neat if liquid or dissolved in a minimum amount of ethanol if solid. If the preprepared catalyst is used, the compound is added to 50 mg of the catalyst in 50 ml of 95% ethanol. The flask is then connected to the Parr hydrogenator and shaken until the theoretical pressure drop for hydrogen is observed. Initial hydrogen pressure was 30 psi in all experiments. The contents of the hydrogenation flask are then centrifuged to separate the catalyst. The decantate was analyzed by gas chromatography. All reaction products were collected and identified by comparison of infrared spectra with those of authentic samples.

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(6) See, *inter alia*, P. N. Rylander, "Catalytic Hydrogenation over Platinum Metals," Academic Press, New York, N. Y., 1967, and references therein.

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Oxidation of *meso*-Tetraphenylchlorins by Dimethyl Sulfoxide to the Corresponding *meso*-Porphyrins[1]

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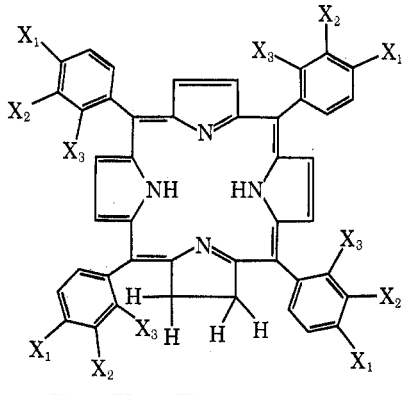
Various meso-tetrasubstituted porphins are prepared by Rothemund synthesis[3–9] but rarely are they obtained chlorin-free.[6] Calvin, *et al.*,[4] separated *meso*-tetraphenylporphin (TTP) from *meso*-tetraphenylchlorin (TPC) by chromatography over talc. This method was later used for purification of similar porphyrins.[8,9] Partial oxidation of chlorins has been achieved with quinones,[10] and selective photooxidative decomposition of zinc chlorins in benzene solution in the presence of quinones followed by chromatography gave pure zinc porphyrins.[9,11] However, these methods of



1, $X_1 = X_2 = X_3 = H$
2, $X_2 = X_3 = H$; $X_1 = CH_3$
3, $X_2 = X_3 = H$; $X_1 = OCH_3$
4, $X_1 = X_3 = H$; $X_2 = OCH_3$
5, $X_1 = X_2 = H$; $X_3 = OCH_3$
6, $X_2 = X_3 = H$; $X_1 = CN$
7, $X_2 = H_3 = H$; $X_1 = NHCOCH_3$

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(2) Undergraduate Research Participant.

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(9) G. M. Badger, R. Alan Jones, and R. L. Laslett, *Aust. J. Chem.*, **17**, 1022 (1964).

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(11) F. M. Huennekans and M. Calvin, *J. Amer. Chem. Soc.*, **71**, 4031 (1949).

TABLE I
ELECTRONIC ABSORPTION SPECTRA OF *meso*-PORPHYRINS TAKEN IN BENZENE SOLUTION[a]

	λ_{max}, mμ (ε × 10⁻³)					
Compd	Soret	IV[b]	III[b]	II[b]	Ia[b]	Ib[b]
1[c]	420 (450)	484 (5.0)	516 (20.7)	550 (8.5)	592 (5.8)	646 (3.8)
1[d]	419 (438)	484 (3.8)	516 (18.4)	549 (8.3)	594 (5.1)	652 (7.4)
1[e]	419 (470)	485 (3.4)	514 (18.7)	549 (7.7)	591 (5.4)	647 (3.4)
1[f]	419 (478)	485 (3.4)	514 (18.7)	548 (8.1)	592 (5.3)	647 (3.5)
1[g]			515 (19.0)	548 (8.0)	592 (5.2)	647 (3.5)
2[c]	420 (558)	483 (6.0)	516 (23.0)	551 (12.0)	594 (6.9)	649 (5.8)
2[d]	421 (478)	484 (5.6)	517 (21.8)	550 (12.6)	595 (6.4)	652 (15.4)
2[f]	420 (490)	485 (3.7)	516 (18.9)	550 (8.2)	592 (5.4)	650 (4.1)
2[h]	420 (485)	485 (4.2)	516 (19.0)	550 (9.7)	592 (5.4)	650 (4.4)
3[c]	423 (410)	486 (4.8)	519 (15.6)	556 (10.2)	596 (5.0)	650 (4.6)
3[d]	424 (385)	488 (3.4)	521 (14.5)	557 (9.7)	598 (4.1)	652 (6.5)
3[e]	424 (408)	488 (3.4)	518 (13.5)	556 (8.9)	595 (4.0)	652 (3.7)
3[f]	424 (485)	488 (4.3)	519 (17.0)	555 (11.9)	595 (5.5)	653 (4.5)
4[c]	422 (480)	485 (5.4)	518 (22.0)	552 (8.1)	594 (6.5)	648 (3.5)
4[d]	420 (357)	483 (3.4)	515 (16.8)	549 (6.5)	594 (4.7)	643 (6.6)
5[c]	421 (568)	482 (7.3)	515 (26.8)	549 (10)	592 (8.3)	648 (4.7)
5[d]	424 (518)	486 (5.2)	518 (19.4)	554 (13)	595 (5.8)	650 (8.6)
5[e]	420 (349)		513 (15.2)	546 (4.6)	590 (4.2)	647 (1.5)

[a] Because of difficulty of solution, compounds **3** and **5** were dissolved initially in pyridine, 0.1 ml for 1 mg of the substance. [b] Numbering of visible absorption bands was done according to J. E. Falk, "Porphyrins and Metaloporphyrins," Elsevier, Amsterdam, London, New York, 1964." [c] Porphyrins purified by the present method. [d] Impure porphyrins obtained by the Rothemund synthesis. [e] From ref 9. [f] From ref 8. [g] From ref 4. [h] From ref 6.

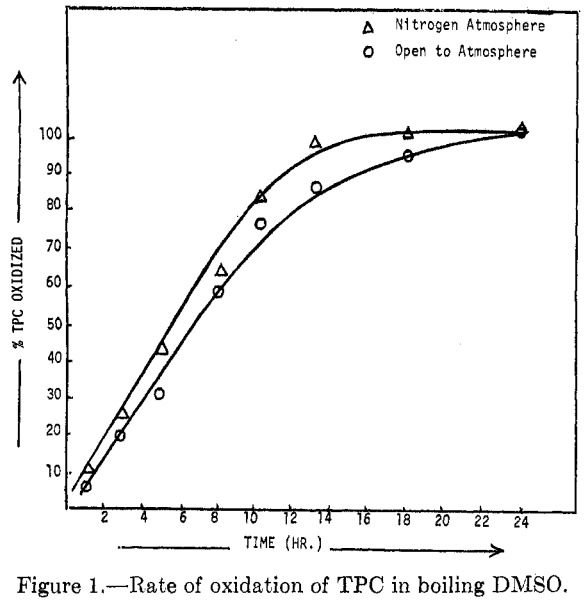


Figure 1.—Rate of oxidation of TPC in boiling DMSO.

obtaining chlorin-free porphyrins are very tedious and time consuming.

This work reports the convenient and quantitative oxidation of several *meso*-chlorins **1–7** in boiling dimethyl sulfoxide (abbreviated as DMSO) to the corresponding *meso*-porphyrins. Spectroscopic measurements show that the *meso*-porphyrins obtained by this method are purer than those obtained by the most reliable chromatographic separation.

Chlorins **1–7** are present as impurities [as high as 10% in the case of TPC (**1**)] in the corresponding porphyrins prepared by the Rothemund synthesis.[5,6] Porphyrins corresponding to chlorins **5** and **7** are new.[12]

Experimental Section

All the solvents used in this work were reagent grade, however, the DMSO was specially purified to free it from any dimethyl sulfone.[13] For spectral measurements a Perkin-Elmer Model 202 ultraviolet–visible absorption spectrophotometer was used. The molar absorbances of pure TPP and pure TPC were obtained from the literature.[4,14] The absorbances at 515 and 650 mμ were used to calculate the per cent of TPP as well as TPC in the reaction mixtures.[15]

Oxidation of *meso*-Chlorins.—*meso*-Porphyrins containing *meso*-chlorins, 0.1 g, were suspended in 100 ml of DMSO and refluxed for 18–24 hr. At different times aliquots of the reaction mixture were diluted with pyridine and the visible absorption spectra were determined. When the intensity of the absorption band near 650 mμ became weaker than the band near 590 mμ and the ratio of the intensity of absorptions at 515–650 mμ remained the same in two successive measurements, the refluxing was discontinued and the porphyrin isolated. The electronic absorption spectra in benzene solution of pure and impure *meso*-porphyrins corresponding to the *meso*-chlorins **1–5** are given in Table I. Spectral data obtained from the literature for porphyrins corresponding to chlorins **1**, **2**, **3**, and **5** are included in this table for comparison.

Effect of Oxygen on the Oxidation of TPC to TPP.—Two experiments were carried out for this. In the first experiment 200 mg of TPP (containing 10% TPC) was refluxed for 24 hr in 200 ml of DMSO (sulfone free) open to the atmosphere. Aliquots of the reaction mixture were periodically taken and the amount of TPC was determined spectrophotometrically. In the second experiment everything was the same except the reaction was carried out under nitrogen atmosphere.[16] The sulfone-free DMSO (100 ml) was freed from dissolved oxygen by bubbling oxygen-free nitrogen for 30 min at 100° and to this was carefully introduced 200 mg of impure TPP and refluxed under nitrogen atmosphere.[16] Aliquots of the reaction mixture were removed also under nitrogen atmosphere for spectral measurements. These operations were done in an all-glass apparatus.

Figure 1 shows the effect of air and nitrogen on the rate of oxidation of TPC by DMSO. It is apparent that atmospheric oxygen is not required for the oxidation.

(12) The synthesis of porphyrins corresponding to chlorins **5** and **7** will be published later.

(13) The DMSO was treated with Atlas Corporation's Darco G-60 (1% for 30 min at room temperature), filtered, and distilled with a fractionating column under nitrogen atmosphere. The final 25% residue was rejected. This method has been obtained by private communication with Crown Zellerbach Corp., Chemical Products Division, Camas, Wash.

(14) G. D. Dorough and F. M. Hunnekans, *J. Amer. Chem. Soc.*, **74**, 3974 (1952).

(15) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy" Wiley, New York, N. Y., 1962, Chapter 20, pp 557–558.

(16) Nitrogen gas of highest purity was freed from trace oxygen by first passing it through a solution of lithium aluminum hydride and benzopinacolone in pyridine (see L. F. Fieser and M. Fieser, "Reagents for Organic Syntheses," Wiley, New York, N. Y., 1967, p 247) and then through a wash bottle containing dry DMSO.

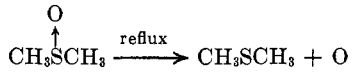
Effect of Temperature on the Oxidation of TPC to TPP.—Four independent oxidation reactions were carried out at temperatures of 150, 165, 175, and 189° (boiling point of DMSO). For each reaction 100 mg of TPP (containing up to 10% TPC) was refluxed for 24 hr in 100 ml of DMSO. The TPP that was isolated from the 175 and 189° reaction did not contain any TPC. The reaction at 165° gave only partial oxidation of TPC and the 150° reaction produced no effect. It was also observed that DMSO decomposed rapidly at 175 and 189°, slowly at 165°, and at no detectable rate at 150°. Therefore, DMSO decomposition is necessary for the oxidation of TPC to TPP.

Attempts to Prepare TPP in One Step. 1.—A mixture of pyrrole (freshly distilled), 0.67 g (0.01 mol), benzaldehyde (distilled), 1.06 g (0.01 mol), and dry DMSO, 100 ml, was refluxed for 48 hr. Although a very low yield of TPP was obtained, the product was completely free from TPC.

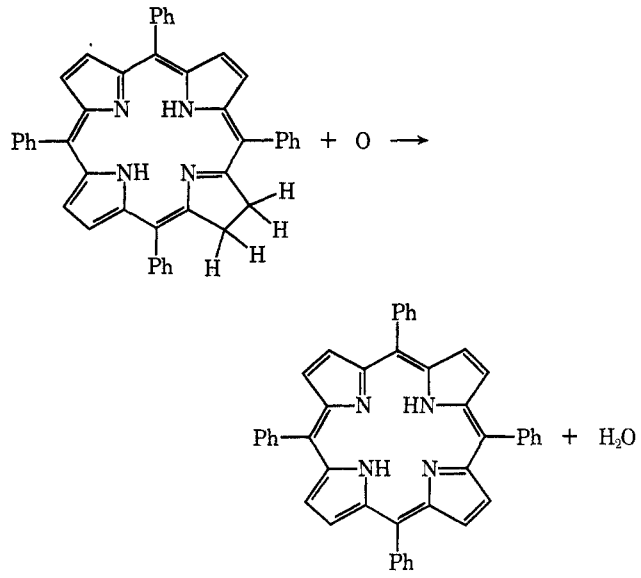
2.—A mixture of pyrrole (freshly distilled), 0.67 g (0.01 mol), benzaldehyde (distilled), 1.06 g (0.01 mol), dry DMSO, 50 ml, and propionic acid, 50 ml, was refluxed for 1 hr. There was a large degree of decomposition producing a dark polymeric product. The reaction mixture did not contain any TPP or TPC.

Discussion

It is known that DMSO decomposes at its boiling point into dimethyl sulfide and oxygen as shown below.



This oxygen atom is a powerful oxidizing agent and has been shown to take part in a number of oxidation reactions.[17] It is this reaction that is responsible for the oxidation of *meso*-chlorins to *meso*-porphyrins as shown in the following equation.



The oxidation scheme proposed above is supported by the already mentioned experiments. Attempts to fit the kinetic data (see Figure 1) to first order and second order with respect to the concentration of TPC were not successful. This may be because the rate of oxidation of TPC depends on the rate of oxidation of DMSO. The effect of temperature on the oxidation supports this view. Further studies to elucidate the mechanism of DMSO oxidation are in progress. It is important to indicate that the *meso*-porphyrins obtained by the present method are highly crystalline and purer than those obtained by other methods (see Table I) which is supported by the higher molar absorbances of *meso*-porphyrins corresponding to the chlorins **1**, **2**, **3**, and **5**.

(17) "Dimethylsulfoxide-Reaction Medium and Reagent," Crown Zellerbach Corp., Chemical Products Division, Camas, Wash., June 1962.

Registry No.—**1**, 917-23-7; **2**, 14527-51-6; **3**, 22112-78-3; **4**, 29114-93-0; **5**, 29114-94-1; **6**, 22112-82-9; **7**, 22220-20-8.

A New Synthesis of Cyclopentenones. Methyl Jasmonate and Jasmone

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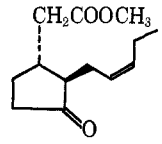
Methyl jasmonate (**1**),[1] a constituent of *Jasminum grandiflorum L.*, has become a valuable raw material in modern perfumery. Despite its importance its chemical synthesis has received little attention. An early synthesis[2] serving mainly to confirm the structure of the odor principle was structurally nonspecific. A more recent[3] synthesis, although elegant, proceeds through intermediates which are difficult to separate from concomitantly formed isomers.



1

We wish to describe an efficient seven-step synthesis of methyl jasmonate (**1**) from dihydroresorcinol (**2**) in 30% overall yield. It was our intention to introduce the acetic acid side chain present in the molecule by addition of a malonic ester to the cyclopentenenone **6** which, in turn, we hoped to prepare by ring contraction of a readily available derivative of cyclohexane. Of the few methods available to effect the latter transformation, the pyrolysis of 2-acetoxy-2-alkylcyclohexane-1,3-diones seemed attractive.[4,5] It proceeds in acceptable yields to give carbon monoxide and 2-alkylcyclopentenones. Unfortunately, this potentially useful method has found no applications because the acetoxydiones, prepared by oxidation of the corresponding β diketones with lead tetraacetate in yields below 20%, remain inaccessible. Although the mechanism of the thermal ring contraction of 2-acetoxy-2-alkylcyclohexane-1,3-diones remains uncertain, Spencer[4] favors the intermediacy of cyclopropanones.[6] Our hope that such cyclopropanones should also be available by elimination of hydrogen chloride from 2-chloro-2-alkylcyclohexane-

(1) E. Demole, E. Lederer, and D. Mercier, *Helv. Chim. Acta*, **45**, 675 (1962).

(2) E. Demole and M. Stoll, *ibid.*, **45**, 692 (1962).

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(4) T. A. Spencer, A. L. Hall, and C. Fordham v. Reyn, *ibid.*, **33**, 3369 (1968).

(5) T. A. Spencer, S. W. Baldwin, and K. K. Schmiegel, *ibid.*, **30**, 1294 (1965).

(6) Cyclopropanones seem to be intermediates also in the thermolysis of 2-acetoxycycloalkanones to cycloalkenes: R. G. Carlson and J. H. Bateman, *ibid.*, **32**, 1608 (1967).