from Aldrich Chemical Co. Cyclohexene (1), methylenecyclohexane (2), 1,3-cyclohexadiene (7), and 1,4-cyclohexadiene (8) were purchased from Chemical Samples Co. Each of the preceding materials was at least 99% pure by GLC. 4-*tert*-Butylmethylenecyclohexane (3) was prepared from 4-*tert*-butylcyclohexanone via the Wittig reaction.[18] Cyclopentadiene (9), obtained from the dedimerization of dicyclopentadiene, was redistilled before use (99.8% by GLC).

Other alkenes which were used as authentic reference compounds for GLC analyses were obtained from Chemical Samples Co.

Other Materials. Benzenesulfonylhydrazide (from Aldrich Chemical Co.) and triethylamine and diglyme (from Matheson Coleman and Bell) were used in diimide reductions as obtained. Potassium azodicarboxylate was prepared by the hydrolysis of azodicarbonamide (Aldrich Chemical Co.).[4] Deuteriomethanol and deuterioacetic acid (99% *O-D*) were obtained from Diaprep Inc.

Reductions with Diimide. The procedure for generating diimide from benzenesulfonylhydrazide was similar to that described by Garbisch et al.[3] Solutions consisting of benzenesulfonylhydrazide (ca. 1.0 g), diglyme (10 ml), triethylamine (ca. 10 g), and either one or two of the unsaturated hydrocarbons (ca. 0.20 g each) were prepared. Eight 1-ml aliquots of the reaction solution were sealed in 8 mm × ca. 15 cm Pyrex tubes. The tubes were kept at 80° by suspending them in either a constant-temperature oil bath or refluxing reagent grade benzene. At appropriate times a tube was removed from the constant-temperature apparatus, cooled in dry ice–2-propanol, and carefully opened. The contents were poured into ca. 1.0 ml of pentane and the pentane extracts were washed twice with 1-ml portions of 5% sulfuric acid, 5% sodium hydroxide, and finally with water. The extracts were dried over magnesium sulfate, sodium sulfate, or Linde 3A molecular sieve and stored in a freezer until analysis by GLC. In those instances where pentane interfered with the product analysis, other solvents such as benzene, toluene, or xylene were used.

Competitive reductions with diimide generated from the decarboxylation of azodicarboxylic acid in methanol at 25° followed the procedure of Baird, Franzus, and Surridge.[4] Reaction solutions consisting of 50 ml of methanol, ca. 1.0 g of a mixture of the two unsaturated hydrocarbons and the internal standard (benzene or toluene), and ca. 3.5 g of potassium azodicarboxylate was stirred in a three-necked flask equipped with a vibrating stirrer (Vibro Mischer), a pressure equalizing addition funnel, and a outlet through which a positive pressure of nitrogen was maintained. A solution of 1.2 g of glacial acetic acid in methanol (15 ml) was added dropwise to the bright yellow reaction mixture. For analysis, a 1-ml portion of the mixture was removed, added to 1 ml of xylene, and washed with small portions of 5% sodium hydroxide and water. The xylene extracts were dried over Linde 3A molecular sieve and analyzed by GLC.

Analytical Procedure. The mixtures were analyzed by GLC (flame ionization detector) on either a 45 ft × 0.125 in. column of 2.5% Carbowax 600 and 2.5% Carbowax 750 on Chromosorb W (AW) 60/80 mesh (for the cyclic dienes and products) or a 25 ft × 0.25 in. column of 30% silver nitrate in triethylene glycol on 60/80 mesh Chromosorb P, which was used for the separations of the alicyclic dienes and products. All peaks were identified by comparison with synthetic mixtures of authentic standards and the molar response factor of each component was determined.[19] The columns were not able to separate 2-methyl-1-butene from 3-methyl-1-butene; however, this did not impair the ability to distinguish 1,2 and 1,4 addition to isoprene (4) because in the analysis on the $AgNO_3$ column 2-methyl-2-butene, the result of 1,4 addition, is cleanly separated from the other components of the reaction mixture.

Reduction of 1,3-Cyclohexadiene with N_2D_2. The deuteriodiimide was generated at 10° in CH_3OD (50 ml) containing the diene (0.4 g) from potassium azodicarboxylate (3.5 g) and deuterioacetic acid (1.2 g) as described by Baird et al.[4] Upon completion of the reaction, the mixture was diluted with water (100 ml) and extracted with three 40-ml portions of pentane. The solution was concentrated to a volume of ca. 5 ml and the concentrate was subjected to preparative chromatography. The ^1H NMR spectrum (Varian A-60) of the cyclohexene which was isolated was integrated and gave a ratio of 2.0:3.1:3.1 for the relative areas of the signals for the vinyl, allyl, and homoallyl protons. The ratio compares well with the value 2:3:3 expected for the product of 1,2 addition and not with the value 2:2:4 expected for 1,4 addition.

Calculations of Relative Rate Constants. A. Competitive Reductions. With the exceptions noted in Table I, the composition of the mixtures from three to six different conversions of the alkenes or dienes were used to compute the relative reactivities, k_A/k_B, from the equation $k_A/k_B = (\log [A]_0 - \log [A])/(\log [B]_0 - \log [B])$ where $[A]_0$ and $[B]_0$ represent the initial mole fractions of A and B, respectively, and [A] and [B] are the fractions when the mixture was sampled.[3]

B. Consecutive Reactions of a Diene. The value of k_2/k_1 (κ), the relative rate constants of the consecutive reactions of a diene → ene → ane, was computed using eq 2 in the form of $(\kappa - 1)\alpha_2 = \alpha_1[1 - \alpha_1^{\kappa-1}]$.[9,10] The value of κ was obtained through successive approximations using a hand-held calculator; the number reported is that for which the ratio of the right- to the left-hand side of the above equation is 1.000 ± 0.002. The precision of the values obtained for different conversions (average deviations) is indicated in Table III.

Registry No.—**1**, 110-83-8; **2**, 1192-37-6; **3**, 13294-73-0; **4**, 78-79-5; **5**, 513-81-5; **6**, 764-13-6; **7**, 592-57-4; **8**, 628-41-1; **9**, 542-92-7; **10**, 142-29-0; **11**, 563-78-0; **12**, 3404-78-2.

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(1) (a) The support of this research by the National Science Foundation is gratefully acknowledged (NSF GP-15719 and NSF GP-3619X). (b) R. P. Fisher and S. E. Johnson were undergraduate research participants (NSF GY-53 and NSF GY-10017).
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Direct Dehydrogenation of Aporphine Alkaloids

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The dehydrogenation of aporphines to the corresponding dehydroaporphines, some of which are naturally occurring alkaloids, has been accomplished by the use of various chemical oxidants, including permanganate, DDQ, mercuric salts, and iodine.[1]

We now report the direct catalytic dehydrogenation of a number of aporphines to dehydroaporphines in high yield and under remarkably mild conditions. The reaction proceeds particularly well in refluxing acetonitrile, using 10% palladium on charcoal catalyst. Under these conditions, nuciferine (1) afforded dehydronuciferine (4) in 90% yield after 15 min reaction time. Other examples of this reaction

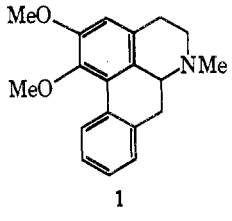
Table I
Dehydrogenation of Some Aporphines to Dehydroaporphines[a]

Aporphine used	(wt, mg)	10% Pd/C, mg	Product	Reaction time, min	Yield,[b] %
Nuciferine (1)	(100)	100	(4)	15	90
Dicentrine (2)	(140)	140	(5)	15	85
Ocopodine (3)	(150)	150	(6)	15	80
Thalicarpine (7)	(140)	140	(8)	60	55

[a] Acetonitrile solvent (10 ml) in all cases. [b] Yields of crystalline products, identical with authentic samples (melting point, ir).[1]

are indicated in Table I. The selective dehydrogenation of the aporphine moiety of thalicarpine (7) is worthy of note. In accord with this result, the simple benzylisoquinoline base laudanosine (9) was recovered unchanged after being subjected to the general dehydrogenation procedure.

The method described here would appear to displace chemical oxidations as the method of choice for the conversion of a nonphenolic aporphine to the corresponding dehydroaporphine. Preliminary dehydrogenation experiments using noraporphines or phenolic aporphines indicate the formation of products which are rapidly attacked by air during work-up, as might be expected from the results of chemical oxidation of similar substrates.[1]



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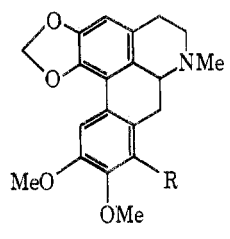

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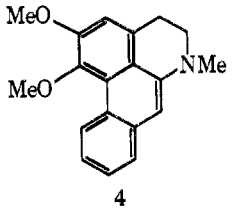

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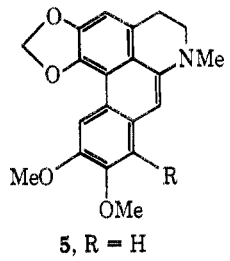
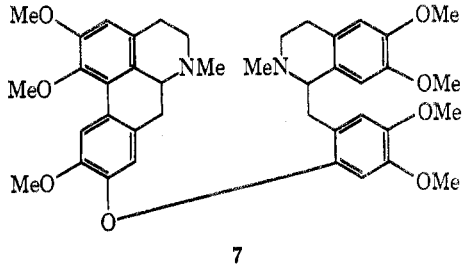


5, R = H
6, R = OMe



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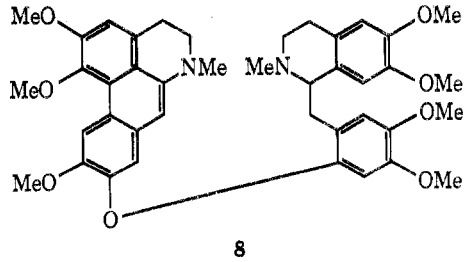

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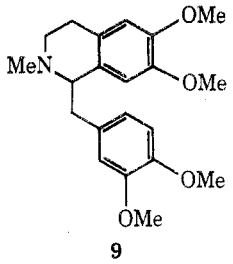

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Experimental Section

In a typical experiment, a mixture of the aporphine (see Table I) and 10% Pd/C in acetonitrile was refluxed under nitrogen for 15 min. The catalyst was filtered off and the solvent was removed in vacuo. The yellow-green residue was crystallized from acetone or methanol. Dehydrothalicarpine (8) was isolated by PLC (silica gel plates, $CHCl_3$ + 10% MeOH), followed by crystallization.

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Registry No.—1, 475-83-2; 2, 517-66-8; 3, 19893-95-9; 4, 7630-74-2; 5, 19843-03-9; 6, 33117-76-9; 7, 5373-42-2; 8, 7224-94-4.

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Novel Rearrangements of Morphanthridines

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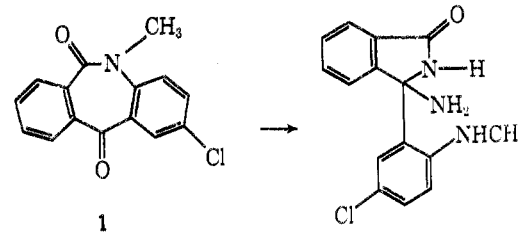
During the course of our investigations toward the synthesis of 9,13b-dihydroisoindolo[2,1-*d*][1,4]benzodiazepin-6-one[1] it was reported that 2-chloro-5-methylmorphanthridine-6,11(5*H*)-dione (1), in the presence of ammonia and NH_4Cl, rearranged in good yield to 3-amino-3-(5-chloro-2-methylaminophenyl)isoindolin-1-one (2). This observation



1 2

prompted further investigations into the possible rearrangements of other morphanthridines functionalized at the 11 position. We now wish to report several successful examples of such rearrangements.

When 2-chlorospiro[morphanthridine-11,2′-oxirane]-6-one (3a) was allowed to react with ammonia in a steel vessel at 120°, it rearranged to form 4-(2-amino-5-chlorophenyl)-3,4-dihydro-4-hydroxyisocarbostyril (4a) in 30% yield (Scheme I). If the morphanthridine was substituted on the nitrogen, e.g., 3b, the reaction proceeded in much higher yield to 4b. Similarly, the treatment of 3a with hydrazine afforded 4-(2-amino-5-chlorophenyl)-3,4-dihydro-4-hydroxy-(2-amino)isocarbostyril (5a) in 50% yield.