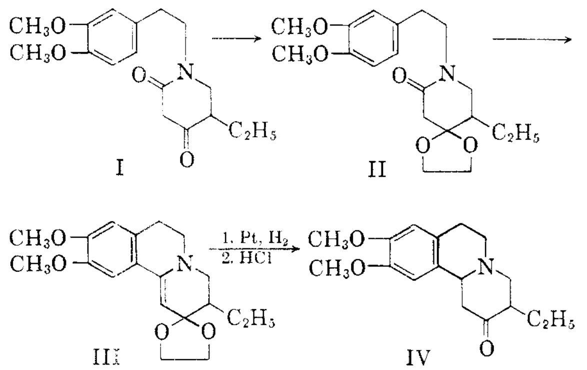
hexahydro-11bH-benzo[a]quinolizine (IV) in a fair yield.



EXPERIMENTAL

1-(3,4-Dimethoxyphenylethyl)-4,4-ethylenedioxy-5-ethyl-2-piperidone (II). A mixture of 5 g. of 1-(3,4-dimethoxyphenylethyl)-5-ethyl-2,4-dioxopiperidine (I)[4] in 150 ml. of benzene, 2 g. of ethylene glycol and 0.2 g. of *p*-toluenesulfonic acid was boiled for 3 hr. surmounted with a constant water separator. On cooling the reaction mixture was shaken with 10% sodium hydroxide solution to remove the starting ketone and toluenesulfonic acid, washed with water, and dried. Benzene was then removed to leave a colorless clear sirup, yield 5 g. (85%), in which the absence of the original ketone was proved by inspection of the infrared spectrum. This was directly used in the next step.

$\Delta^{1:11}$*-2,2-Ethylenedioxy-9,10-dimethoxy-3,4,6,7-tetrahydro-2H-benzo[a]quinolizine* (III). To a boiling solution of 1 g. of the foregoing compound in 50 ml. of pyridine was added an intimate mixture of 5 g. of phosphorus pentoxide and 50 g. of purified sea sand in 4 portions with stirring.[5] After being refluxed for 6 hr. altogether the pyridine solution was decanted while still hot and the resultant residue was extracted with 3 × 10 ml. portions of hot pyridine. Pyridine was distilled from the combined pyridine solution. The residue was mixed with 10 ml. of benzene, which was distilled off to remove the residual pyridine. This manipulation was repeated twice more, thus leaving 0.7 g. of a reddish brown sirup, which was characterized as the picrate, yellow prisms from ethanol, m.p. 109–110°.

Anal. Calcd. for $C_{25}H_{28}O_{11}N_4$: C, 53.6; H, 5.0; N, 10.0. Found: C, 53.6; H, 5.2; N, 10.3.

2-Oxo-3-ethyl-9,10-dimethoxy-1,2,3,4,6,7-hexahydro-11bH-benzo[a]quinolizine (IV). A solution of 0.5 g. of aforementioned crude base in 20 ml. of ethanol, acidified with a few drops of 10% hydrochloric acid, was hydrogenated over platinum catalyst, 53 ml. of hydrogen being absorbed. One-half g. of a colorless sirup thus obtained was dissolved in a few ml. of 10% hydrochloric acid and warmed on a steam bath for 1 hr. The solution was filtered through a wet filter paper and the filtrate was made alkaline with potassium carbonate with cooling. The base that separated was taken up in benzene and dried, and the solvent was removed to leave 0.43 g. of a colorless glass, which solidified on standing. This formed colorless needles from *n*-hexane, m.p. 109°, which was not depressed on admixture with an authentic sample prepared according to the method of Battersby *et al.*,[2a] yield 0.2 g. The total yield from II was 31%.

The picrate formed yellow prisms from ethanol, m.p. 182–183° (decomp.).

Anal. Calcd. for $C_{25}H_{26}O_{10}N_4$: C, 53.3; H, 5.0; N, 10.8. Found: C, 53.65; H, 5.3; N, 10.7.

Acknowledgment. The authors are grateful to Mr. M. Nakamura, vice-president of Yawata Chemical Industries Ltd., for a generous donation of pure pyridine.

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[4] Y. Ban, *Pharm. Bull.* (*Japan*), **3**, 53 (1955).

[5] After some time stirring became impossible through caking.

Synthesis of 1-*p*-Methoxybenzyl-1,2,3,4,5,6,7,8-octahydroisoquinoline

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Received June 25, 1959

1-Substituted 3,4,5,8-tetrahydroisoquinolines are precursors of 1,2,3,4,5,6,7,8-octahydroisoquinolines, which, when suitably substituted in the 1-position, form key intermediates for the synthesis of morphinans. Bischler-Napieralski cyclization of *N*-acyl-2-(1,4-cyclohexadienyl)ethylamine to yield 1-substituted 3,4,5,8-tetrahydroisoquinolines has been described by the present authors.[2]

We now report the acylation of 2-(1,4-cyclohexadienyl)ethylamine with *p*-methoxyphenylacetyl chloride to form the corresponding amide which was then cyclized to give 1-*p*-methoxybenzyl-3,4,5,8-tetrahydroisoquinoline. Since the latter is unstable in air it was catalytically reduced without purification to yield 1-*p*-methoxybenzyl-1,2,3,4,-5,6,7,8-octahydroisoquinoline. The identity of the latter was confirmed by a mixed melting point with an authentic sample prepared according to the procedure of Schnider and Hellerbach.[3] It was converted to 3-hydroxy-*N*-methylmorphinan by the method of these authors.

EXPERIMENTAL

N-2-(1,4-Cyclohexadienyl)ethyl-p-methoxyphenylacetamide. 2-(1,4-Cyclohexadienyl)ethylamine (6.2 g.) in 80 ml. of benzene was treated with *p*-methoxyphenylacetyl chloride (9.4 g. in benzene) in the presence of sodium bicarbonate (5%, 200 ml.) with cooling and stirring. An oily amide was obtained, which solidified on scratching and was purified from a mixture of *n*-hexane and benzene, colorless scales, m.p. 86–86.5°, yield 12.5 g. or 92%.

Anal. Calcd. for $C_{17}H_{21}O_2N$: C, 75.3; H, 7.75; N, 5.2. Found: C, 75.5; H, 7.7; N, 5.1.

1-p-Methoxybenzyl-1,2,3,4,5,6,7,8-octahydroisoquinoline. A mixture of *N*-2-(1,4-cyclohexadienyl)ethyl-*p*-methoxyphenylacetamide (3 g.), phosphoryl chloride (3 ml.) and benzene (50 ml.) was refluxed for 30 min., giving a reddish yellow solution, a copious evolution of hydrogen chloride being observed. On cooling enough petroleum ether was added to the reaction solution to produce a reddish precipitate, which

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[1] Present address: No. 40, 3-chome, Iogi, Suginami-ku, Tokyo, Japan.

[2] S. Sugasawa and R. Tachikawa, *Tetrahedron*, **4**, 205 (1958).

[3] O. Schnider and J. Hellerbach, *Helv. Chim. Acta*, **33**, 1437 (1950).

was separated from the supernatant liquid after some time and dissolved in dilute hydrochloric acid. The acid solution, after being shaken with benzene and filtered through a wet filter paper, was made alkaline cautiously with caustic soda solution with cooling and stirring. The benzene layer was washed and dried and the solvent was removed in vacuo in a hydrogen atmosphere. The reddish residue thus obtained was dissolved in methanol (50 ml.) and reduced over Raney nickel (1.5 g.), *ca.* 2 molar equivalents of hydrogen being absorbed. The catalyst and the solvent were removed and the residue was dissolved in benzene and purified through an alumina column. After evaporation of the solvent there remained a yellow oily base, which was again dissolved in methanol, neutralized with hydrobromic acid and evaporated. The residue solidified on scratching and was purified from a minimum amount of hot water (charcoal) to give the hydrobromide salt of 1-*p*-methoxybenzyl-1,2,3,4,5,6,7,8-octahydroisoquinoline as colorless prisms, m.p. 197–198°, undepressed when admixed with an authentic specimen, yield 1.55 g. or 41.3%. Both specimens also gave the identical IR spectra.

Anal. Calcd. for $C_{17}H_{23}ON \cdot HBr$: C, 60.4; H, 7.1; N, 4.1. Found: C, 60.0; H, 6.7; N, 4.1.

Catalytic reduction of the 2-methyl quaternary salt of the tetrahydro base did not give a satisfactory result. Methylation was accomplished by catalytic reduction in the presence of formaldehyde and the 1-*p*-methoxybenzyl-2-methyl-1,2,3,4,5,6,7,8-octahydroisoquinoline was converted to 3-hydroxy-*N*-methylmorphinan, m.p. 250–252°, by the procedure of Schnider and Hellerbach.[3] Its identity was confirmed by mixed melting point with an authentic sample.

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Pyrolysis of 1,1-Dichloro-2-vinylcyclopropane. Synthesis of 2-Chlorocyclopentadiene

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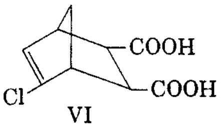
The reaction of chloroform with butadiene in the presence of potassium *t*-butoxide gives 1,1-dichloro-2-vinylcyclopropane (I).[1] This material is remarkably stable, being resistant to the action of bases, to zinc and magnesium in refluxing ethanol or tetrahydrofuran and is not attacked by molecular oxygen.[2] However, on vacuum pyrolysis at about 500° (5 mm. nitrogen atmosphere), the compound was converted essentially completely to a mixture of new chloroolefins. Low temperature vacuum distillation of the mixture permitted isolation in about 90% purity of a monochlorocyclopentadiene (II) which on the basis of its Diels-Alder reactions was concluded to have the chlorine atom in the 2- position.

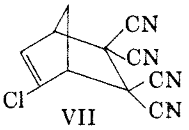
Vapor phase chromatography of the reaction product on a silicone column resulted in separation into four major peaks and several additional minor ones. While the structures of these materials have not been conclusively demonstrated, evidence was obtained for the existence of 4,4-dichlorocyclopentene (III), 1,1-dichloropenta-1,4-diene (IV), and 1,1-dichloropenta-1,3-diene (V) in the pyrolysis mixture.

Evidence for the interesting chlorocyclopentadiene structure consisted of hydrogenation with palladium on charcoal in alcoholic potassium hydroxide to cyclopentane; a mass spectrum indicating a molecular weight of 100 and the presence of one chlorine atom (from the size of the isotopic 102 peak); the infrared spectrum showing a strong band at 6.3μ attributable to a conjugated diene structure; the nuclear magnetic resonance spectrum which showed the presence of two types of hydrogens in the ratio of 3 to 2 with resonance at +9.0 and +42.5 parts per ten million from benzene, respectively; the ultraviolet spectrum with maxima at 254 (ϵ 3200) and 250 (ϵ 3200) with a shoulder at 238 (ϵ 2500) mμ; the exothermic reactions with maleic anhydride and tetracyanoethylene; and the spontaneous dimerization of the material on standing.

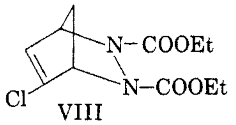
The conclusion that the molecule reacted as if the chlorine atom were in the 2- rather than the 1-position on the cyclopentadiene ring was made on the basis of the absence of the 14.2μ *cis*-hydrogen band in the infrared spectra of all the Diels-Alder derivatives which were prepared. This band was present in all authentic bicyclo(2,2,1)hept-5-ene derivatives unsubstituted in the 5- and 6-positions which were examined.



VI



VII



VIII

In addition, the nuclear magnetic resonance (NMR) spectrum of VI showed the presence of four kinds of hydrogens in the approximate ratios of 4:2:2:1. The lone hydrogen atom had its resonance peak at the position of resonance of the olefinic hydrogens in bicyclo(2,2,1)hept-5-ene-2,3-dicarboxylic acid. The existence of a dynamic equilibrium between 1- and 2-chlorocyclopentadiene with more rapid reaction of the 2- isomer cannot be ruled out, however, though an attempt to find even a small amount of an isomeric adduct in the maleic anhydride reaction was unsuccessful.

The evidence for the 4,4-dichlorocyclopentene (III) consisted of the infrared, NMR, and mass spectrum of a fraction which had been collected by vapor phase chromatography. Also in a series of

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[1] R. C. Woodworth and P. S. Skell, *J. Am. Chem. Soc.*, **79**, 2542 (1957).

[2] All of these observations are in sharp contrast to the behavior of 1,1-dibromo-2-vinylcyclopropane, N. P. Neureiter, unpublished results; see also W. E. Doering and P. M. LaFlamme, *Tetrahedron*, **2**, 75 (1958).