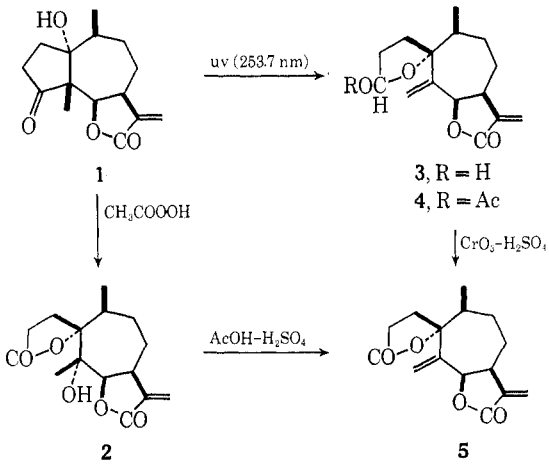
SCHEME I



silica gel (35 g) packed in ether–$CHCl_3$ (2:3). Elution of the column with the same solvent yielded 140 mg of crude photocoronopilin-A (**3**). Further elution of the column recovered 79 mg of coronopilin (**1**). Photocoronopilin-A (**3**) had the following: mp 93–97° (from isopropyl ether); $[\alpha]^{25}D$ −105° (*c* 0.53, EtOH); uv (EtOH) λ_{max} 211 mμ (ε 8900); ir ($CHCl_3$) 3600–3500 (hydroxyl), 1752 (carbonyl), 1655 and 1640 cm^{-1} (double bonds); nmr (ppm, δ scale) 5.4–5.6 (H_4 and H_6), 4.90 and 5.32 (c, $C_5 = CH_2$), 3.15 (c, H_7), 0.87 (C_{10}-Me, d, J = 7 Hz) and 0.90 (C_{10}-Me, d, J = 7 Hz), 5.56 (m, $H_{13a \text{ and } b}$) and 6.23 ($H_{13a \text{ and } b}$, d, J = 2 Hz), 6.24 (d, J = 2 Hz), and 3.5 (c, OH). *Anal.* Calcd for $C_{15}H_{20}O_4$: C, 68.14; H, 7.63; O, 24.21. Found: C, 68.03; H, 7.54; O, 24.14.

Acetylation of **3** with acetic anhydride and pyridine under standard conditions yielded the acetate **4** as an oil: nmr 6.2 (m, H_4), 4.83 and 5.28 (c, $C_5 = CH_2$), 5.22 (H_6, d tr, J = 10 and 1.5 Hz), 3.17 (c, H_7), 0.87 (C_{10}-Me, d, J = 7 Hz), 5.50 ($H_{13a \text{ and } b}$, d, J = 2.2 Hz), 6.15 (d, J = 2.4 Hz), and 1.97 (s, acetyl-Me).

Anhydropsilostachyin (5) from Photocoronopilin-A (3).—A solution of 40 mg of **3** in 1 ml of acetone was treated at room temperature with three drops of the CrO_3–H_2SO_4 reagent.[8] After a half minute, the mixture was diluted with 10 ml of water and extracted with two 3-ml portions of CH_2Cl_2. The CH_2Cl_2 extract was washed (aqueous $NaHCO_3$) and dried (Na_2SO_4). The crystals obtained upon evaporation of the solvent were recrystallized from isopropyl ether–acetone: yield of **5**, 25 mg; mp 158°. The specimen was identical with an authentic sample of anhydropsilostachyin prepared from psilostachyin[3] (**2**) by nmr, ir, and mixture melting point.

Registry No.—**3**, 26823-94-9; **4**, 26823-95-0.

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Isolation and Chemistry of the Invertomers of *N*-Chlorobenzoylphenylaziridine

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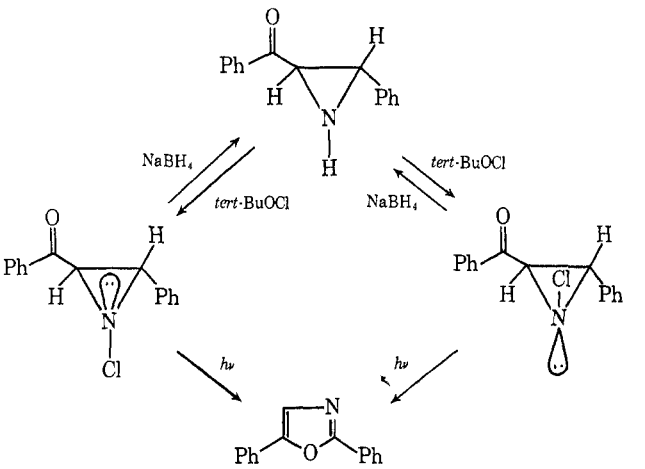
Recent nmr studies have shown that inversion about nitrogen is a relatively slow process for *N*-haloaziridines.[2–4] The high energy barrier for inversion has been ascribed to a combination of inductive and electrostatic factors which stabilize the pyramidal configuration.[2,5] In fact, the rate of pyramidal inversion about nitrogen is sufficiently slow to permit separation of the two invertomers in the cases of 7-chloro-7-azabicyclo[4.1.0]heptane[5] and *N*-chloro-2-methylaziridine.[6,7] At this time we wish to disclose our results on the preparation of the two invertomers of *N*-chlorobenzoylphenylaziridine as well as to report on some of the chemical properties of this system.

Treatment of *trans*-benzoylphenylaziridine with *tert*-butylhypochlorite in methylene chloride at 25° for 2 hr afforded a mixture of the two invertomers of *N*-chlorobenzoylphenylaziridine (Ia and Ib). A clean separation of the two components could be achieved by thick layer chromatography. The structure of these materials was established by elemental analysis, as well as by ir and nmr spectra. The mass spectra of both components show a peak at *m/e* 222 which corresponds to the loss of chlorine from the parent peak. The nmr spectrum of the fast moving component, mp 86–86.5°, shows an AB quartet at τ 5.80 (J = 5.8 Hz) while the slow moving component, mp 83.5–84°, has the AB quartet located at τ 5.91 (J = 5.5 Hz). Both components revert back to *trans*-benzoylphenylaziridine on reduction with sodium borohydride in methanol.



As part of our continuing probe into the excited state behavior of small ring ketones, we attempted to dehydrochlorinate I in order to study the photochemistry of the benzoylphenylazirene system. Preliminary efforts to dehydrohalogenate either aziridine were unsuccessful. All attempts led to the formation of *trans*-benzoylphenylaziridine.

In view of Gassman's recent results on the solvolysis of *N*-chloroaziridines,[7] it was expected that I would solvolyze at a rapid rate. However, both aziridines could be recovered unchanged from a silver nitrate–methanol solution. Thus it would appear that this

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particular *N*-chloroaziridine system is reluctant to form a nitrenium ion and undergo ring cleavage. This might be attributed to the presence of the electron deficient benzoyl group attached to the adjacent carbon atom.

Irradiation of a solution of Ia (or Ib) in benzene at 25° in a Pyrex immersion apparatus with a 450-W Hanovia lamp for 7 hr led to complete disappearance of starting material. Conventional isolation procedures afforded 2,5-diphenyloxazole in high yield. The formation of the oxazole and the complete absence of the isooxazole ring suggest that the reaction proceeds by exclusive C–C bond scission. Subsequent ring closure to a 2,3-dihydrooxazole followed by dehydrochlorination readily accounts for the observed product.

Experimental Section

***N*-Chloro-2-benzoyl-3-phenylaziridine (Ia and Ib).**—To a solution of 2.0 g of 2-benzoyl-3-phenylaziridine[8] in 50 ml of methylene chloride was added 2.0 g of *tert*-butyl hypochlorite. After stirring for 2 hr at room temperature, the solvent was removed under reduced pressure and the crude solid was subjected to preparative thick layer chromatography.[9] Elution with benzene afforded two bands which were taken up in acetone. Removal of the solvent from the lower band gave material with mp 83.5–84°.

Anal. Calcd for $C_{15}H_{12}ClNO$: C, 69.89; H, 4.69; N, 4.45; Cl, 13.75. Found: C, 69.71; H, 4.75; N, 5.52; Cl, 13.73.

The nmr spectrum showed an AB quartet centered at τ 5.91 (J = 5.5 Hz) and a multiplet centered at τ 2.20 (10 H). Removal of the solvent from the upper band of the thick layer plate gave an isomeric material, mp 86–86.5°.

Anal. Calcd for $C_{15}H_{12}ClNO$: C, 69.89; H, 4.69; N, 5.45; Cl, 13.75. Found: C, 69.75; H, 4.75; N, 5.50; Cl, 13.73.

The nmr spectrum showed an AB quartet at τ 5.80 (J = 5.8 Hz) and a multiplet for the aromatic hydrogens.

Photolysis of *N*-Chloro-2-benzoyl-3-phenylaziridine.—A solution of 1.0 g of Ia (or Ib) in 1 l. of benzene was irradiated with an internal water-cooled mercury arc lamp (450-W) using a Pyrex filter. After 7 hr the solution was concentrated to give a brown oil. The residue was dissolved in benzene and chromatographed on a Florisil column. Elution with benzene gave 2,5-diphenyloxazole (80%) as white needles. Further elution of the column afforded only ill-defined tars.

Attempted Dehydrohalogenation and Solvolysis of *N*-Chloro-2-benzoyl-3-phenylaziridine.—In a typical case, 0.10 g of I was dissolved in 10 ml of methanol. To the above solution was added 5 ml of a 10% sodium methoxide–methanol solution. The mixture was allowed to stir for 12 hr. The resulting solution was washed with water, extracted with CH_2Cl_2, and dried (Na_2SO_4). Removal of the solvent under reduced pressure, followed by infrared and nmr analysis showed the presence of only *trans*-benzoylphenylaziridine. Similar results were obtained when sodium hydride, phenyl lithium, 1,5-diazabicyclo[4.3.0]non-5-ene, and potassium *tert*-butoxide were used as bases.

In an attempt to investigate the solvolytic behavior of I, a 0.10-g sample of I was added to a 10% aqueous methanol solution containing 0.85 g of silver nitrate. The resulting solution was allowed to stir for 12 hr at room temperature. The solvent was removed under reduced pressure and the residue was dissolved in benzene and washed with water, and the extracts were dried. Removal of the solvent showed only the presence of unreacted starting material.

Registry No.—1a, 26823-97-2; 1b, 26823-98-3.

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(9) Thick layer plates were prepared by spreading a slurry of 150 g of Merck $HH_{254+366}$ silica gel and 350 ml of water onto 10 × 20 cm glass plates to an average thickness of 1.5 cm. The plates were allowed to dry at room temperature for 24 hr.

Stereochemistry of the Palladium-Catalyzed Hydrogenation of 3-Oxo-4-ene Steroids. III. The Effects of the Functional Groups at C-11, C-17, and C-20 on the Hydrogenation[1,2]

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It has been previously reported from our laboratories that during the hydrogenation of 4-cholesten-3-one (**9**) and testosterone (**3a**) with palladium catalyst in alcohols, acetic acid, or in these solvents containing mineral acid, a larger amount of 5β ketone was formed from **9** than from **3a**. In comparison with **3a**, testosterone acetate (**3b**) gave the 5β ketone in considerably higher yield. Such an increase in the yield of 5β ketone on changing a 17β-hydroxyl group to a 17β-acetoxyl group was also observed in the corresponding compounds of the 19-nor series, which led to the suggestion that the effect of a 17β-hydroxyl group is to decrease the formation of 5β ketones.[2,4] Such influence of substituents, which lie far from the reaction site, on the stereochemistry of hydrogenation has already been noted by Pataki, Rosenkranz, and Djerassi[5] during the hydrogenation of 11β-hydroxy- and 11-oxo-substituted 3-oxo-4-ene steroids, and similar observations were made by other investigators[6,7] while our work was in progress. It seems rather difficult to explain these phenomena in terms of steric effect alone.

With the aim of getting more quantitative and systematic information on the influence of functional groups on hydrogenation, we have now hydrogenated 25 3-oxo-4-ene steroids with or without functional groups at C-11, 17, or 20 over prereduced palladium hydroxide. Products were analyzed by gas–liquid chromatography.

The results are given in Table I. From the Table it is seen that 17β-acetoxy-11β-hydroxy-4-androsten-3-one (**5**), 11β-hydroxy-4-androstene-3,17-dione (**7a**), and 11β-hydroxyprogesterone (**15a**), which are all 3-oxo-4-ene steroids containing an 11β-hydroxyl group, afford apparently rather different ratios of 5β to 5α ketone. However, when the results are compared with those for

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