**Nitration of I.**—To 0.2 ml of I (191 mg, 1.46 mmoles) and 221 mg (2.2 mmoles) of $KNO_3$ was added 2–3 ml of HF, and the reaction was conducted as described above. The infrared spectrum of the reaction product showed a double carbonyl band, at 5.65 and 5.75 $\mu$, as expected for II.[11] The infrared spectrum of I exhibits a broad carbonyl absorption at 5.8–6.0 $\mu$.

Analysis by vapor phase chromatography was performed on a 3% Carbowax 20 M column, 15 ft × 1/8 in. at 120°. Under these conditions I has a retention time of 1.0 min, while II is retained for 1.8 min. The reaction mixture showed only these two peaks. The ratio of II to I was 93:7.

**Denitration of II.**—A mixture of 0.2 ml of II (225 mg, 1.27 mmoles) and 0.2 ml of anisole (199 mg, 1.84 mmoles) was allowed to react in 2–3 ml of HF as described above. The reaction mixture exhibited an infrared absorption band at 5.8–6.0 $\mu$, the expected carbonyl absorption band for I. Vapor phase chromatography under the conditions detailed above showed a peak at 0.3 min, attributable to anisole, and a peak at 1.0 min owing to I. No peak was detected at 1.8 min, the position expected for II.

The nitroanisoles are retained on the column under the conditions used to separate I and II. They were separated on a 20% Carbowax 20 M column, 9 ft × 1/8 in. at 200°. Under these conditions *o*-nitroanisole appears at 22 min and *p*-nitroanisole at 25 min. These two compounds were both identified in the reaction mixture by their retention times. The ratio of *o*-nitroanisole to *p*-nitroanisole was 70:30.

**Nitration of III.**—To 348 mg of III (2 mmoles) and 303 mg (3 mmoles) of $KNO_3$ was added 7 ml of HF. The reagents were dissolved in the HF by stirring and allowed to react as described above. Amino acid analysis of the reaction mixture showed that quantitative conversion to nitroarginine had occurred. No arginine was detected, nor were any other ninhydrin-positive products except nitroarginine. The product was then recovered from water (adjusted to pH 6 with $NH_4OH$ and acetic acid) in 83% yield, and recrystallized once from hot water: $[\alpha]^{25}D$ +26.2° (*c* 2.9, 1 *N* HCl), $\lambda_{max}$ 271.6 m$\mu$ ($\epsilon$ 15,000) in dimethylformamide–0.2 *N* HCl (1:1); lit. $[\alpha]^{25}D$ +24.3° (*c* 4.12, 2 *N* HCl),[12] 271.6 m$\mu$ ($\epsilon$ 15,595) in dimethylformamide–0.2 *N* HCl (1:1).[13]

**Denitration of IV.**—A mixture of 58.1 mg of IV (26.5 $\mu$moles) and 0.1 ml of anisole (100 mg, 0.92 mmole) was allowed to react in 2–3 ml of HF as described above. The reaction mixture was taken up in 25 ml of 0.01 *N* HCl, chilled, and filtered to remove traces of insoluble material. Some of this solution (0.5 ml) was subjected to automatic amino acid analysis. Only one peak appeared, in the position normally occupied by III. Calculation of its area showed it to contain 0.51 ± 0.02 $\mu$mole (97 ± 4%) of III.

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## Synthesis of 9-(2′-Deoxy-β-D-ribopyranosyl)adenine

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In the previous paper[1] 9-(tetrahydro-2-pyranyl)-adenine was shown to be prepared easily from adenine and 2,3-dihydro-4H-pyran. In the present work, by using 3,4-di-O-acetyl-D-arabinal in place of 2,3-dihydro-4H-pyran, 9-(2′-deoxy-β-D-ribopyranosyl)adenine was obtained.

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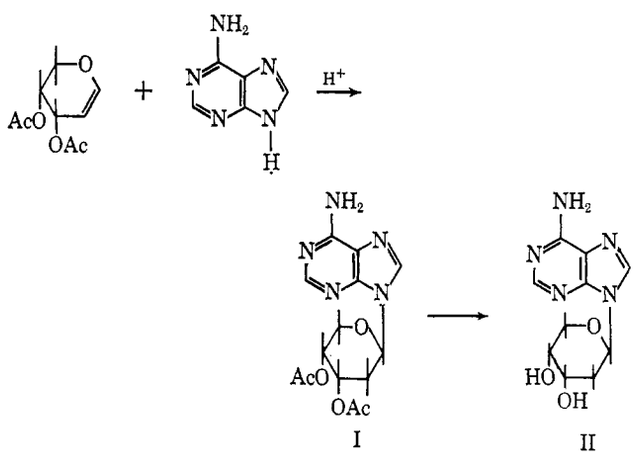
Adenine was treated with 3,4-di-O-acetyl-D-arabinal in dimethyl sulfoxide in the presence of a small excess of hydrogen chloride. The product was separated on an alumina column and 9-(2′-deoxy-3′,4′-di-O-acetyl-D-ribopyranosyl)adenine (I) was obtained. The sugar moiety of I was assigned to position 9 by comparison of its ultraviolet absorption spectra with those of 9-substituted adenines. The ultraviolet absorption spectra of I at pH 1 and 11 show maxima at 257 and 260.5 m$\mu$, respectively, very similar to those of adenosine at 259 (pH 1) and 261 (pH 11) and 9-methyladenine at 260 (pH 1) and 260 (pH 11), in contrast to those of 7-methyladenine at 272 (pH 1) and 270 (pH 11) and 3-methyladenine at 274 (pH 1) and 273 m$\mu$ (pH 11).[2] Deacetylation of I gave a compound (II), mp 267–268°, $[\alpha]^{23}D$ −16.5 (*c* 0.53, water). Compound II was shown to be identical with 9-(2′-deoxy-β-D-ribopyranosyl)adenine prepared by Zinner[3] [mp 262–264°, $[\alpha]^{20}D$ −17.8 (*c* 0.58, water)] and by Robins[4] [mp 266–267°, $[\alpha]^{26}D$ −17.0 (*c* 0.6, water)]. It is of interest that the 9-β derivative (I) was the predominant isomer formed from adenine and 3,4-di-O-acetyl-D-arabinal with hydrochloric acid. When 6-chloropurine was treated with glycal in the presence of *p*-toluenesulfonic acid, Robins[5] found that the α anomer, 6-chloro-9-(2′-deoxy-3′,4′-di-O-acetyl-α-D-ribopyranosyl)purine, was the main product.




I II

### Experimental Section

**9-(2′-Deoxy-3′,4′-di-O-acetyl-β-D-ribopyranosyl)adenine (I).**—Four grams of adenine (0.03 mole) was dissolved in 40 ml of dimethyl sulfoxide with 7 ml of a solution of hydrogen chloride in dry dioxane (5 *N*). To the solution 8 g of 3,4-di-O-acetyl-D-arabinal[6] was added at 50° with stirring. The mixture was kept at 50° for 15 hr, made basic with ammonium hydroxide, and concentrated under reduced pressure. The residue was treated with acetone. After the residual adenine (3 g, 0.02 mole) was filtered, the filtrate was applied to an alumina column and eluted with acetone–ethanol (ethanol: 0, 5, 10, 50%). From the fraction of acetone, a yellow oil was obtained. From the fraction of 10% ethanol–acetone, 0.7 g (0.002 mole) of I was obtained. Recrystallization of I from ethanol gave colorless needles, mp 218.5–219°. Ultraviolet absorption at pH 1 showed $\lambda_{max}$ 257 m$\mu$ ($\epsilon$ 14,800); at pH 11 it showed $\lambda_{max}$ 260.5 m$\mu$ ($\epsilon$

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14,300); in ethanol it showed $\lambda_{max}$ 261 mμ (ε 16,300) and 230 mμ (shoulder).

*Anal.* Calcd for $C_{14}H_{17}N_5O_5$: C, 50.14; H, 5.11; N, 20.89. Found: C, 50.41; H, 5.38; N, 20.76.

**9-(2′-Deoxy-β-D-ribopyranosyl)adenine (II).**—In 20 ml of absolute methanol, 0.33 g of I was dissolved and 3.2 ml of a solution of barium methoxide in methanol (1 *N*) was added. The mixture was kept at room temperature overnight and refluxed for 40 min. The solution was neutralized with carbon dioxide. The precipitate was filtered off and the filtrate was concentrated under reduced pressure. Recrystallization of the residue from water gave II, mp 267–268°, $[\alpha]^{23}D$ −16.5 (*c* 0.53, water). Ultraviolet absorption at pH 1 showed $\lambda_{max}$ 258 mμ (ε 15,000); at pH 11 it showed $\lambda_{max}$ 261 mμ (ε 14,600); in ethanol it showed $\lambda_{max}$ 260.5 mμ (ε 16,000) and 231 mμ (shoulder).

*Anal.* Calcd for $C_{10}H_{13}N_5O_3$: C, 47.8; H, 5.2; N, 27.9. Found: C, 47.74; H, 5.45; N, 27.84.

## The Reaction of Diphenylcyclopropenone with Alkaline Hydrogen Peroxide

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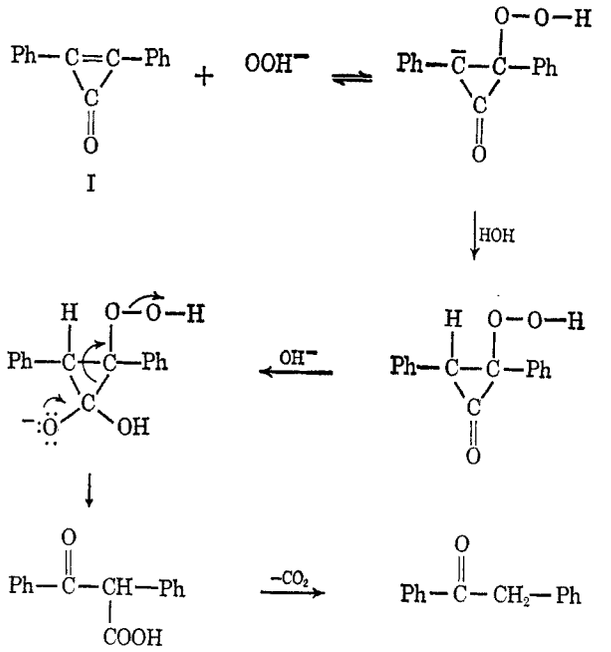
Although the preparation of bicyclobutane or derivatives has been reported,[2] the heterocyclic analog, oxabicyclobutane, or its derivatives have never been made. Epoxidation of diphenylcyclopropenone (I) appeared to be a convenient method for the preparation of a derivative of oxabicyclobutane.

The reaction of diphenylcyclopropenone with hydrogen peroxide and sodium carbonate or sodium hydroxide afforded desoxybenzoin as the major product. A small amount of an intensely yellow, oily material, which was not identified, was also produced. Breslow, *et al.*,[3,4] have found that I reacts with alcoholic sodium hydroxide to form *cis*-1,2-diphenylpropenoic acid, indicating an initial attack of hydroxide ion on the carbonyl carbon atom. It is postulated that the hydroperoxide ion, on the other hand, reacts at the carbon–carbon double bond, as in the case of an "ordinary" α,β-unsaturated carbonyl compound.[5] However, the succeeding steps, in which ring closure to the epoxide is effected, could not take place because of unfavorable steric factors. Consequently, an alternate pathway is followed; one possible route is depicted in Scheme I.

Attempts were made to oxidize diphenylcyclopropenone with peroxyacetic acid but in each instance the starting material was recovered unchanged. Reaction of I with hydroxylamine resulted in the formation of desoxybenzoin oxime[4] as one of the products, which points to the involvement of the carbon–carbon double bond, rather than the carbonyl group, in the first step. Attempts to oxidize I with hypochlorite ion (in aqueous dioxane) were unsuccessful, starting material

SCHEME I




being recovered each time. The hypochlorite–pyridine reagent[6] was ineffective because of the rapidity of the reaction of I with the pyridine.[4]

### Experimental Section

**Reaction of Diphenylcyclopropenone with Alkaline Hydrogen Peroxide.**—To a solution of 2 g (0.01 mole) of diphenylcyclopropenone[4] in 25 ml of purified dioxane was added 4 ml of 3 *M* NaOH (or 10 ml of 5% $Na_2CO_3$). Two milliliters of 25% hydrogen peroxide was then added dropwise to the stirred mixture. The temperature of the reaction mixture was maintained at 25–30° during the addition and for 30 min thereafter. The addition of 60 ml of ice–water caused the separation of a yellow solid, which was filtered and allowed to air dry. The yield of the crude product was 1.5 g. Recrystallization from methanol afforded white crystals, mp 55–56°, whose infrared spectrum was identical with that of an authentic sample of desoxybenzoin.

The mother liquor from the recrystallization was evaporated and the residual solid was recrystallized again. After another such operation a yellow, oily residue (less than 0.5 g) remained.

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## Preparation of Ethyl α-Aryloxyacetoacetates and the Decomposition of Ethyl α-(4-Acetylphenoxy)acetoacetate

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Several ethyl α-aryloxyacetoacetates have been described in the literature as intermediates in the preparation of benzofurans and naphthofurans.[1] Among the analogous compounds (**1a** to **1f**) prepared in this laboratory was ethyl α-(4-acetylphenoxy)acetoacetate (**1c**). It was observed that this compound, originally ob-

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