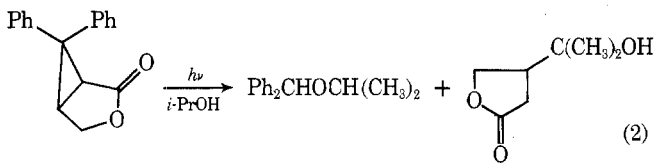


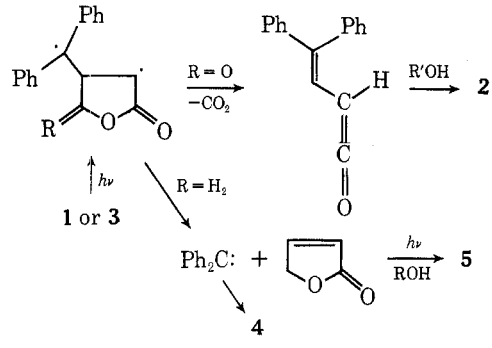
(2)

3 4 5

Both of these reactions can be rationalized in terms of cyclopropane bond homolysis to produce trimethylene diradicals.[1,6] In the case of the anhydride, cycloelimination of carbon dioxide would then lead to the formation of an unsaturated ketene which should capture solvent to give the observed product. This is depicted in Scheme I.

The diradical derivable from 3 cannot eliminate CO_2 in the same fashion and thus may fragment to diphenylcarbene and the unsaturated lactone. This olefin is known[5] to add isopropyl alcohol photochemically in the manner depicted in Scheme I.

Scheme I



It should be noted that the evidence presented here does not require the intermediacy of a diradical. Hixson[7] has shown that a cyclopropane closely related to those described here fragments stereospecifically to produce the diphenylcarbene and an olefin in a process that, as in these reactions, originates only from the singlet excited state.

Experimental Section

General. Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Proton magnetic resonance spectra were recorded on a Varian Associates T-60 instrument with tetramethylsilane as the internal standard. Irradiations were conducted using a 450-W Hanovia lamp in a quartz immersion well. Irradiation solutions were deoxygenated by bubbling nitrogen through them for 1 h before and then during irradiation. Isopropyl alcohol was distilled from magnesium just before use. *tert*-Butyl alcohol was distilled from potassium.

Irradiation of 6,6-Diphenyl-3-oxabicyclo[3.1.0]hexane-2,4-dione (1). A solution of 284 mg (1.07 mmol) of 1[2] in 330 ml of *tert*-butyl alcohol was irradiated for 4 h using a Vycor filter. After solvent removal the NMR spectrum of the photomixture indicated that the major component of the mixture was starting material, but that there was an additional absorption signal at δ 3.07. This material was dissolved in 100 ml of ether, stirred with 100 ml of water, and the organic layer washed with 10% sodium carbonate solution. The ether solution was dried and the solvent removed. The residue was chromatographed on a 2.5 × 190 cm column slurry packed in hexane; 50-ml fractions were collected. Elution was accomplished with 250 ml of hexane and then 1 l. each of 5 and 10% ether–hexane. Fractions 27–34 contained 25 mg of a yellow oil. Attempted crystallization of this oil from chloroform–hexane afforded 18 mg (57% based on recovered starting material) of a clear oil. This material was identified as (1,1-dimethyl)ethyl 4,4-diphenylbut-3-enoate by comparison with the authentic ester synthesized from the known acid.[4] The photoproduct ester was dissolved in cyclohexane containing several drops of sulfuric acid and a white precipitate formed in several minutes. This solid was recrystallized from cyclohexane to afford 13 mg of 4,4-diphenylbut-3-enoic acid, mp 116–117 °C, mmp with authentic[4] acid 116–118 °C (lit.[4] mp 114–115 °C). The NMR spectrum ($CDCl_3$) is δ 9.8 (br, 1 H, COOH), 7.1–6.9 (m, 10 H), 5.97 (triplet, 1 H, J = 6 Hz), 3.07 (doublet, 2 H, J = 6 Hz). The spectrum of the *tert*-butyl ester was identical with the exception of the absence of the acid proton resonance and the presence of the *tert*-butyl group absorption at δ 1.43 (singlet, 9 H). Acidification of the sodium carbonate wash afforded 271 mg of a mixture of the *cis*- and *trans*-3,3-diphenyl-1,2-cyclopropanedicarboxylic acids.[2] A similar irradiation of 1 using 10.0 ml of acetone (0.136 mol) as a sensitizer and a Corex light filter gave no detectable reaction in a 12-h irradiation.

6,6-Diphenyl-3-oxabicyclo[3.1.0]hexan-2-one (3). A solution of 1.80 g (9.28 mmol) of diphenyldiazomethane[8] in 100 ml of dry benzene was added dropwise over 0.5 h to a solution of 2.00 g (23.8 mmol) of 2 (5*H*)-furanone[9] in 100 ml of dry benzene at room temperature. This material was heated at reflux for 4 h and the solvent removed in vacuo. The oily product mixture was chromatographed on a 2.5 × 87.5 cm column of Florisil slurry packed in hexane; 50-ml fractions were collected. Elution was with 500 ml of hexane and 500-ml portions of 2, 4, 8, and 15% ether–hexane. Fractions 23–25 contained 610 mg of an oil. Crystallization from ether–hexane afforded 458 mg (20%) of 3, mp 136–137 °C. Spectral data were uv (CH_3OH) 274 nm (ϵ 34), 268 (59), 261 (60), 254 (49); NMR ($CDCl_3$) δ 2.80 (multiplet, 2 H), 4.25 (m, 2 H), 7.1 (m, 10 H); MS (50 ev) *m/e* (rel intensity) 250 (31) (M^+), 205 (100), 165 (68); ir (KBr) 1775 (sh), 1750 (sh), 1195, 700 cm^{-1}.

Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.88; H, 5.69.

Irradiation of 6,6-Diphenyl-3-oxabicyclo[3.1.0]hexan-2-one (3). A solution of 301 mg (1.20 mmol) of 3 in 330 ml of isopropyl alcohol was irradiated for 4 h using a Vycor filter. After solvent removal most of the starting material was crystallized from ether–hexane, 268 mg, mp 135–137 °C. The residue was then separated by gas chromatography (156 °C, 20% SE-30 on firebrick in a 5 ft × 0.25 in. column, flow rate 60 ml He/min) to give 24 mg of isopropyl benzhydryl ether (4) (retention time 2.7 min) and 15 mg of 4-(1′-hydroxy-1′-methylethyl)-4,5-dihydro-2(3*H*)-furanone (5) (retention time 21 min). The identities of these materials were confirmed by the superimposability of their ir and NMR spectra upon those of independently synthesized materials. The ether 4 was made by a standard method[10] and the hydroxy lactone prepared by the irradiation of 2(5*H*)-furanone[9] as reported by Ohga and Matsuo.[5] A similar irradiation of 3 in which 10 ml of the solvent was replaced by acetone as a sensitizer afforded no reaction after 12 h of irradiation.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. The partial support by the Research Corporation and by the Research Initiation Award program of the Cleveland State University are also acknowledged with pleasure. We thank Professors Binkley and Andrist for their help and encouragement.

Registry No.—1, 26844-85-9; 2, 58540-89-9; 2 free acid, 7498-88-6; 3, 58540-90-2; diphenyldiazomethane, 883-40-9; 2(5*H*)-furanone, 497-23-1.

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A Phosgeneless Synthesis of Diaryl Carbonates

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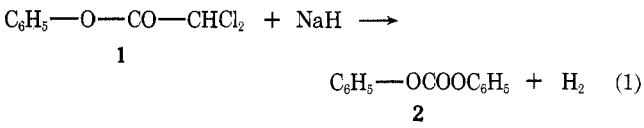
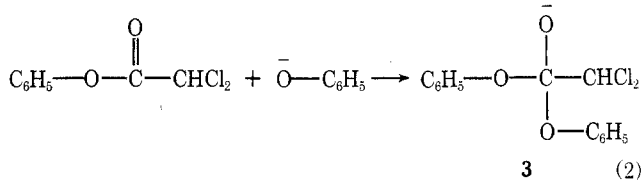
The production of diaryl carbonates most often involves at some point the use of extremely toxic phosgene. In this

paper we report the synthesis of carbonates without the use of phosgene by employing esters of dichloroacetic acid. The overall reaction is shown in reaction 1 for phenyl dichloroacetate.

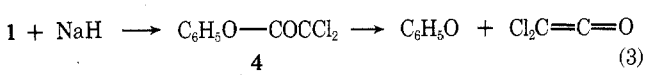


This reaction is unusual in that it results in an oxidative cleavage of C–C bonds apparently brought about by sodium hydride. The yield of diphenyl carbonate was modest, 35–70%, and was accompanied by formation of tar and phenol along with dichloroacetic acid on water workup of the reaction mixture.

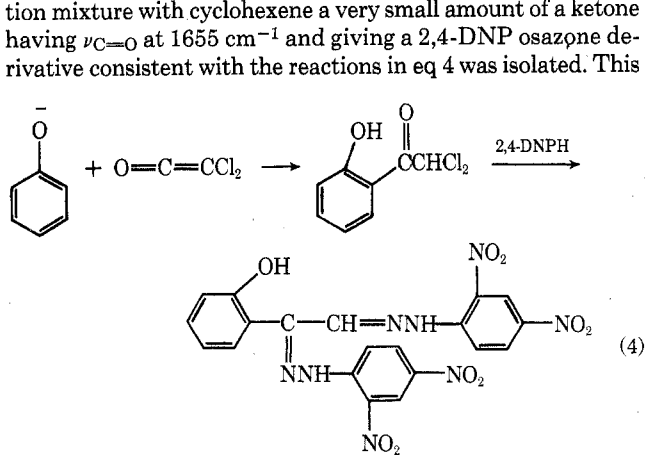
A reasonable mechanism would involve attack of phenoxide, as in eq 2, on the carbonyl.



This attack would be followed by expulsion of $CHCl_2$ from **3** or a concerted expulsion of Cl^- and :CHCl such as has been reported[2] in the reaction of dichloroacetophenone with *tert*-butoxide. Indeed, it was found that phenoxide ion cleaved the phenyl dichloroacetate to give diphenyl carbonate in 60% yield, thus implicating phenoxide as in reaction 2. With carefully purified phenyl dichloroacetate, having literature[3] values for physical constants, and containing no detectable phenol by GC, reaction 1 gave diphenyl carbonate in yields up to 71%, indicating that the ester must be the source of the phenolate ion. Reaction 3 shows that phenolate ion could be plausibly generated by expulsion of dichloroketene from the ester after abstraction of a proton (reaction 3).

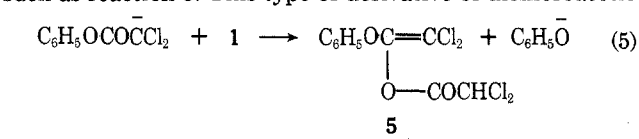


Attempts to trap dichloroketene with cyclohexene[6] or cyclopentadiene[7] were not successful. However, from the reaction mixture with cyclohexene a very small amount of a ketone having $\nu_{C=O}$ at 1655 cm^{-1} and giving a 2,4-DNP osazone derivative consistent with the reactions in eq 4 was isolated. This



2,4-dinitrophenylosazone was identical with one obtained from an authentic 2-hydroxy-α,α-dichloroacetophenone prepared by a Fries rearrangement of the phenyl dichloroacetate.[4] Such osazone formation is typical behavior for α,α-dichloroacetophenones and has long been known.[5] The failure to trap dichloroketene with dienes or 2,3-dimethyl-2-butene could be considered a serious argument against this mechanism. However, as we show below, from consideration of the mass balance in alternate mechanisms, dichloroketene expulsion must be fairly important; and the isolation of this ketone and the vinyl dichloroacetate ester described below must indicate generation of dichloroketene. Apparently dichloroketene is reluctant to attack even a very electron-rich aromatic ring such as phenolate ion and instead undergoes alternate fates expected of it.

The source of phenolate ion could also be considered a path such as reaction 5. This type of derivative of dichloroacetic



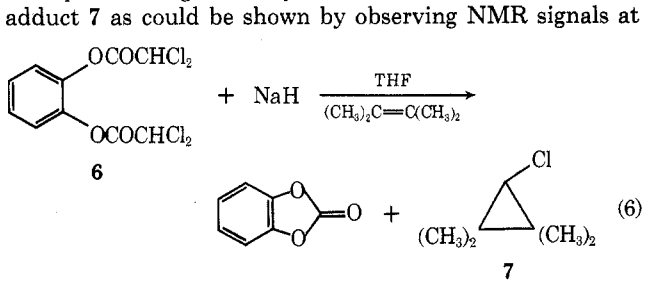
acid was found by Lavanish when he treated excess dichloroacetyl chloride with triethylamine.[8] Such behavior toward enolate ions seems to be typical of haloketenes.[9]

When 1 was treated with one-half stoichiometric amounts of sodium hydride in THF and the solvent removed, there was obtained an oily solid which had two strong ir bands at 1780 and 1640 cm^{-1}. These bands were attributed to the carbonyl and the C=C bond in **5** in the reaction mixture. Attempts to distill this mixture led to gas evolution, and the only distillable materials obtained were phenol, starting ester, and a trace of diphenyl carbonate. Apparently **5** decomposes with expulsion of dichloroketene to give starting ester.

A chromatographic attempt was made to isolate compound **5** by chromatography on silica gel. After elution of all the reaction mixture components (see Experimental Section), a band of organic material remained at the top of the column. When this was eluted with acetone an oily semisolid was obtained which had ir bands at 1770–1790 cm^{-1} and a band at 1640 cm^{-1} and NMR signals at δ 6.05 and 5.90 ppm and a multiplet at 7.33 ppm. The signals at 6.05 and 7.33 ppm are due to the presence of starting ester, as was confirmed from examination of the infrared spectrum (see Experimental Section). The signal at 5.90 ppm we attribute to the presence of compound **5**. Furthermore, at the time of isolation the 6.05/5.90 ratio was 9/8, but in 3 h it had risen to 6.05/5.90 = 9/4. These data are consistent with the postulate that **5** is unstable relative to starting ester and dichloroketene. Reinforcement for this view comes from the realization that the starting ester was removed from the chromatography column in the second fraction and the material examined here was removed in the 12–16 fraction.

Reaction 5 cannot be solely responsible for the generation of phenolate ion because it would require 3 mol of ester to produce 1 mol of diphenyl carbonate. This would make our yields in the neighborhood of 110%. This means that, in spite of the failure of dienes to trap it, dichloroketene must be expelled in the formation of phenolate ion. The dichloroketene is then trapped by phenolate ion as *o*-hydroxydichloroacetophenone, and as **5** by the enolate **4**. Apparently in the presence of enolate ions this is the preferred fate for dichloroketene rather than addition to double bonds.

Following an unsuccessful attempt to trap monochlorocarbene and/or chloroform from phenyl dichloroacetate we sought to trap chlorocarbene from the bisdichloroacetate ester of catechol (eq 6) in the presence of 2,3-dimethyl-2-butene. This procedure gave low yields of the alkene–halocarbene adduct **7** as could be shown by observing NMR signals at



0.9–1.3 ppm. The cyclopropane **7** is known to display a sharply defined doublet centered at 1.25 ppm, due to chemically shifted methyl groups, and a sharp singlet at 2.70 ppm. Both of these signals are observable in the reaction mixture from reaction 7. Further evidence for the presence of **7** was found by observing a GC retention time (see Experimental Section) identical with authentic **7**.

In view of the failure to trap methylene chloride, even with phenol in the reaction mixture, we ascribe the appearance of chlorocarbene to a concerted expulsion of chloride and chlorocarbene from the intermediate ion **3** in reaction 2. This is quite consistent with the known behavior of dichloroacetophenone[2] and contrasting with haloform cleavages observed in trihalogenated esters.[11]

The reaction of bisdichloroacetate catechol ester, **6**, with sodium hydride in THF led to a smooth production of *o*-phenylene carbonate in 60–70% yield. The material obtained was identical with an authentic sample prepared by distillation of *o*-hydroxyphenylethyl carbonate.[12]

The synthetic usefulness of the reaction was explored briefly with the 3,5-dimethylphenol ester and the *p*-bromophenyl ester, which gave yields of 41.5 and 54%, respectively.

Experimental Section

Instrumental. All infrared spectra were measured on a Perkin-Elmer Model 700 spectrophotometer; NMR spectra were obtained on a Varian EM 360 and melting points with a Mel-Temp block, and they are uncorrected. Gas chromatography was performed on a Varian Model 920 with columns as noted. Elemental analysis was performed by Galbraith Laboratories.

Phenyl Dichloroacetate (1). This compound was made by allowing phenol and dichloroacetyl chloride to react using triethylamine as an acid scavenger. Distillation followed by recrystallization from petroleum ether–ether gave solid white crystals, mp 46–48 °C (lit.[2] 48 °C). Gas chromatography on a 20 ft × 0.375 in. SE-30 on 30/60 Chromosorb W showed 99+% purity.

Reaction of Phenyl Dichloroacetate with Sodium Hydride. In a typical procedure a three-necked 250-ml flask equipped with a mechanical stirrer, dropping funnel, and reflux condenser was charged with 5.0 g of sodium hydride (50% dispersion in mineral oil). This was washed three times with 25 ml of dry benzene, then covered with 50 ml of dry tetrahydrofuran and 20 g (0.092 mol) of the phenyl dichloroacetate in 25 ml of dry THF was added slowly under N_2 with vigorous stirring. A lively evolution of hydrogen ensued and the solution turned red, then brown and began to reflux gently. When gas evolution ceased, the flask was stirred for 0.5 h further. Then the brown solution was poured into 300 ml of 3 N hydrochloric acid, immediately extracted with three 100-ml portions of dichloromethane, and dried over magnesium sulfate. Solvent removal left a red oil which was picked up in methylene chloride and washed with 10% sodium bicarbonate until the aqueous layer was clear. Distillation of this oil gave, after a leading fraction containing 2.8 g of phenol and one containing 1.68 g of ester, 7.2 g of diphenyl carbonate. This represents a yield of 70.8% based on 2 mol of ester consumed per mole of carbonate produced.

Catechol Bis(dichloroacetate) (6). This compound was prepared by the reaction of catechol with dichloroacetyl chloride. Typically 11.0 g (0.1 mol) of catechol was dissolved in 200 ml of benzene and 15 ml of dry diethyl ether in a three-necked mechanically stirred 1-l. flask equipped as for phenyl dichloroacetate. To this mixture 29.7 g (0.2 mol) of dichloroacetyl chloride was added and stirring was begun. A solution of 20.2 g (0.2 mol) of triethylamine in 100 ml of dry benzene was added dropwise over a 2-h period and stirring was prolonged for an additional 1 h after addition was complete.

Filtration of the suspended salt after this period gave only 8.5 g of amine salt. Subsequently the organic filtrate was washed with two 150-ml portions of 4 N hydrochloric acid and with three 100-ml portions of water. After drying over $MgSO_4$ and solvent removal, distillation (100–110 °C, 0.5 Torr) gave a solid, mp 64.5–66 °C, which was the diester, and a liquid which was the monoester (bp 70–75 °C, 0.55 Torr). The yield of solid was 65%, and the liquid was 11.5%. The solid diester was characterized by absence of ν_{OH} at 3600–3300 cm^{-1} and presence of a strong $\nu_{C=O}$ at 1770 cm^{-1} and ν_{C-O} at 1138 cm^{-1} (strong). The NMR spectrum ($CDCl_3$, vs. Me_4Si) had two strong singlets at δ 6.11 (2 H) and 7.33 (4 H).

Anal. Calcd for $C_{10}H_6O_4Cl_4$: C, 36.18; H, 1.82. Found: C, 36.15; H, 1.86.

Reaction of Catechol Bis(dichloroacetate) with Sodium Hydride. A 3.3-g (0.01 mol) sample of this diester was treated with 0.48 g (0.01 mol) of NaH in a 50% oil dispersion as described for phenyl dichloroacetate. An immediate reaction occurred which consumed the NaH in 1 min. The solution was stirred overnight and worked up with hydrochloric acid as before. The organic layer after drying and solvent removal gave 1.18 g of a solid, mp 119–120 °C, after recrystallization from ether, 60% yield. This material was identical in infrared spectroscopy [$\nu_{C=O}$ at 1780 (broad) and 1850 cm^{-1} (sh)],[13] and NMR spectroscopy (signal at δ 7.22 ppm, singlet), and physical properties to a sample of *o*-phenylene carbonate made by distillation of *o*-hydroxyphenylethyl carbonate.[12] The NMR of the authentic material showed complete absence of signals besides a singlet at δ 7.22.

When this reaction was run in the presence of 5.0 g of 2,3-dimethyl-2-butene and worked up as recorded above, the NMR spectrum in $CDCl_3$ of the reaction mixture showed signals due to chemically shifted methyl groups centered at δ 1.25 (doublet) and a sharp singlet at 2.70 ppm. These signals were similar to signals obtained from an authentic sample of **7** obtained by the method of Closs[10] (−5 °C, slow addition of butyllithium to a CH_2Cl_2 solution of 2,3-dimethyl-2-butene). Gas chromatography of the reaction mixture after removal of most of the tetrahydrofuran by distillation showed a peak at 3.6-min retention time on a 20 ft × 0.375 in. 15% SE-30 on 30/60 Chromosorb W column (column temperature 132 °C, He flow 80 ml/min). This was the identical retention time with that of the authentic sample under identical conditions.

***o*-Hydroxy-α,α-dichloroacetophenone.** This ketone was prepared by a Fries rearrangement of phenyl dichloroacetate as outlined in ref 4. There was obtained a 50% yield of a colorless to pale yellow liquid on distillation (bp 65–72 °C, 0.1 Torr)[7] which gave a 2,4-dinitrophenylosazone on warming with 2,4-DNPH in sulfuric acid–ethanol, mp 263–265 °C.

Anal. Calcd for $C_{20}H_{14}N_8O_9$: C, 47.07; H, 2.76; N, 21.95. Found: C, 46.92; H, 2.61; N, 21.86.

Trapping Experiment with Cyclohexene. A sample of 2.2 g of 50% sodium hydride in oil was washed with three 50-ml portions of dry benzene, then covered with 50 ml of dry cyclohexene and cooled to 0 to −5 °C, with ice–salt water and stirred vigorously as 20 g (0.0922 mol) of phenyl dichloroacetate was added, in 120 ml of cyclohexene, over a period of 0.5 h. After stirring for an additional 1 h, the reaction was quenched with water, and the organic phase separated and distilled. The second, third, and fourth fractions contained a ketone (bp 45–50 °C, 0.01 Torr) which gave a 2,4-DNP osazone derivative, mp 258–261 °C, ir $\nu_{C=O}$ 1650–1660 cm^{-1}.

Anal. Calcd for $C_{20}H_{14}N_8O_9$: C, 47.07; H, 2.76; N, 21.95. Found: C, 46.66; H, 3.10; N, 21.96.

The yield was less than 1% of the theoretical for this ketone.

These data are essentially those of the authentic ketone obtained from Fries rearrangement of phenyl dichloroacetate.

Isolation of Compound 5. To a 10-g (0.046 mol) sample of phenyl dichloroacetate in 100 ml of THF was added 1.0 g (0.023 mol) of sodium hydride washed free of oil. This mixture was allowed to stir for 2 h, and the solvent was removed after this time. The reaction mixture displayed a broad carbonyl band from 1790 to 1775 cm^{-1} and a medium-strong band at 1640 cm^{-1}. Distillation gave a fraction at 65–87 °C (2.0 Torr) which was mostly starting material. At 99–118 °C at 0.4–1.2 Torr three fractions were obtained along with gas evolution; these fractions were also all starting material. Finally, at 124–180 °C along with gas evolution there was obtained still another fraction of mostly starting ester. The material giving the 1640-cm^{-1} band was not obtained in this distillation although much gas evolution, presumably dichloroketene, occurred.

This experiment was repeated using 22 g of ester and 2.18 g of sodium hydride. A 3.5-g sample of the reaction mixture was chromatographed on 60–200 mesh silica gel to obtain 2.02 g of starting ester in the first five fractions (ether–50% petroleum ether). The sixth and seventh fractions (60% ether–petroleum ether) contained 25–30 mg of a red oil leaving $\nu_{C=O}$ at 1650 cm^{-1} and ν_{OH} at 3400 cm^{-1} (presumed to be the hydroxyacetophenone of reaction 4). In the 12th through 16th fractions (40% acetone–100% acetone, ethyl acetate) there was obtained an oily semisolid having $\nu_{C=O}$ at 1770 and 1640 cm^{-1}. The 1770-cm^{-1} band had a shoulder at 1780–1785 cm^{-1}. The NMR spectrum had signals at δ 6.05 (singlet) and 5.90 (singlet) (ratio of 9:8), as well as an aromatic multiplet at 7.3–7.1 ppm. After standing for 3 h, the upfield singlet diminished and the 6.05/5.90 ratio was 9.8/4.0.

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Registry No.—1, 10565-20-5; 2, 102-09-0; 5, 58462-98-9; 6, 58462-99-0; 6 monoester analogue, 58463-00-6; 7, 14123-41-2; catechol, 120-80-9; dichloroacetyl chloride, 79-36-7; o-phenylene carbonate, 2171-74-6; o-hydroxy-α,α-dichloroacetophenone, 29003-58-5; o-hydroxy-α,α-dichloroacetophenone bis(2,4-dinitrophenylosazone), 58463-01-7; 2,4-DNPH, 119-26-6.

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Nucleosides. 98. Direct Introduction of an Acetamido Group into the Sugar Moiety of Nucleoside Epoxides[1]

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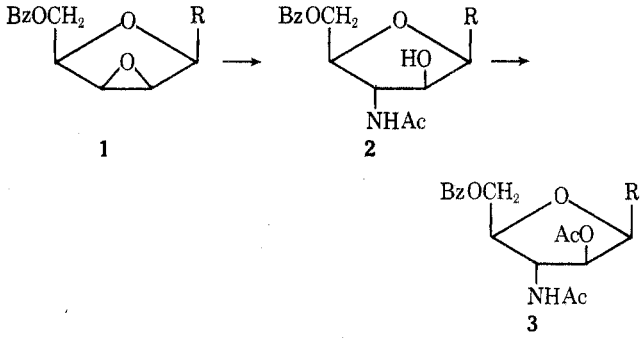
The interest in the synthesis of aminoglycosides (including amino nucleosides) has grown over the years owing to the antibiotic properties that many of them exhibit.[2] The most common method for the introduction of an amino group into a sugar is via nucleophilic displacement of a sulfonyloxy group by azide followed by reduction[3] or by opening an epoxide by ammonia.[4] In the case of nucleosides, an amino group may be introduced into the carbohydrate moiety by cyclization of nucleoside dialdehydes with nitromethane followed by reduction of the nitro group,[5] by replacement of a sulfonyloxy group,[6] or by opening an epoxide[7] or 2,2′-anhydro linkage[8] with azide and subsequent reduction of the azido function. Direct opening of nucleoside 2′,3′-epoxides with ammonia is also known.[9] We report herein a facile method for the *direct* introduction of an acylamino group into the sugar moiety of nucleosides by the use of boron trifluoride etherate in acetonitrile.

Treatment of the nucleoside 2′,3′-epoxides (**1**) with boron trifluoride etherate in acetonitrile followed by neutralization of the reaction mixture with saturated sodium hydrogen carbonate solution gave the corresponding 3′-acetamido-3′-deoxyarabinosyl nucleosides (**2**) which crystallized out in pure state from the reaction mixture (Chart I).

A plausible mechanism for the conversion of **1** → **2** via postulated intermediates **4** and **5** is shown (Chart II). This mechanism is somewhat akin to that proposed by Smith et al.[10] for the synthesis of oxazolines from epoxides. In the case of nucleoside 2′,3′-epoxides, however, anchimeric assistance from the 2′ oxygen in zwitterion **5** to form an oxazoline cannot occur. Hydrolysis of **5** results in the formation of 3′-acetamido-3′-deoxyarabinosyl nucleosides (**2**). It is noteworthy that TLC examination of the product **2** showed only one spot; no evidence for the formation of a 2′-acetamidoxylo nucleoside was obtained.

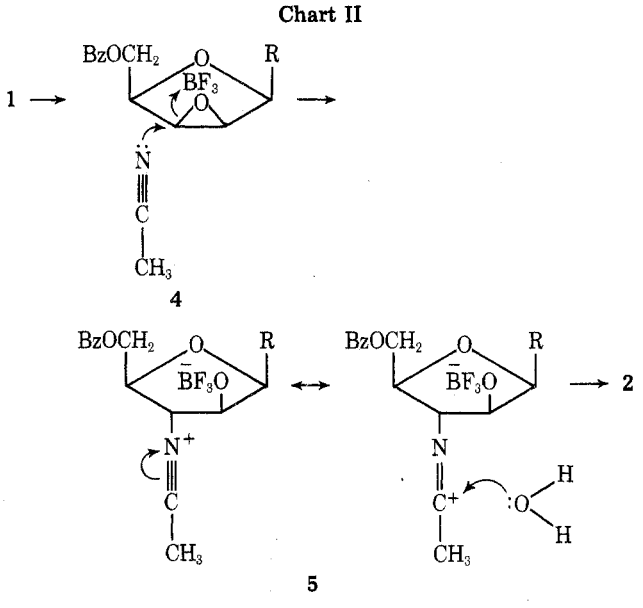
Chart I



1 2 3

a, R = uracil b, R = N^4-benzoylcytosine

Chart II



The structures of nucleosides **2** were established in the following manner: the position of the free hydroxyl group at C-2′ was confirmed by acylation of **2** to **3**, followed by NMR analyses of the acetylated products. In nucleosides **3** the sugar ring protons geminal to the acetoxy group are shifted downfield by ~1.2 ppm relative to their chemical shift in the parent compounds **2** (see NMR data in Experimental Section) and now appear as a triplet. Irradiation at the frequency of the triplet converted the doublet of the anomeric proton signal into a singlet. Upon irradiation at the frequency of the anomeric signal, the above mentioned triplet became a doublet. These decoupling experiments firmly allocate the hydroxyl substituent to C-2′ and, consequently, the acetamido function to C-3′ in **2** and **3**. Final proof was achieved by an unambiguous synthesis of 1-(3-acetamido-2-*O*-acetyl-5-*O*-benzoyl-3-deoxy-β-D-arabinofuranosyl)uracil and its identity with **3a** by NMR, ir, and mixture melting point. Thus, the lyxo epoxide **1a**[11] was treated with ammonium azide to afford **6** which was hydrogenolyzed to amino nucleoside **7** and acetylated to **3a** (Chart III).

Application of the boron trifluoride etherate–acetonitrile reagent combination to 2′,3′-epoxides of purine nucleosides is planned in our laboratory.

Experimental Section

NMR spectra were obtained on a JEOL J1M-PET-100 spectrometer with Me_4Si as reference. Chemical shifts are reported in parts per