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Photolysis of Nitrate Esters. Photochemically Initiated Inversion of Configuration

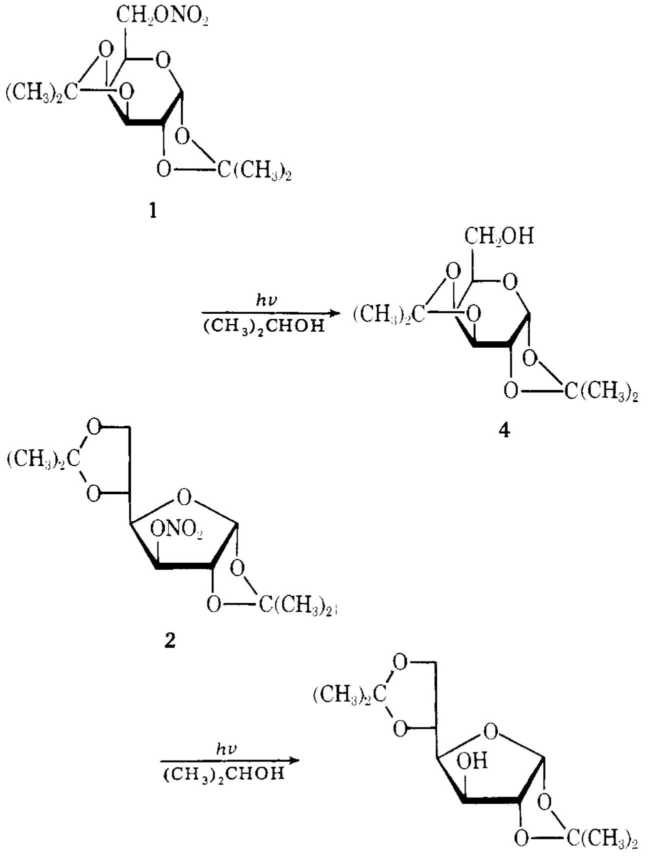
Summary: Photolysis of nitrate esters **1** and **2** in 2-propanol results in the formation of the corresponding alcohols while photolysis of nitrate ester **3** produces an alcohol with inverted configuration.

Sir: Nitrate esters of carbohydrates are compounds which are stable in the presence of a variety of reagents;[1] thus, they can be effective hydroxyl protecting groups, although they are used less frequently for this purpose than groups such as acetals, ketals, and carboxylic acid esters. One factor which limits the use of nitrate esters is the relatively vigorous conditions for their removal, which typically require heating with a nucleophile such as hydrazine or treating with a reducing agent such as lithium aluminum hydride.[1] The information available on the photolysis of nitrate esters suggests that alkoxy radicals are produced upon irradiation;[2] thus, irradiation in the presence of hydrogen donors is potentially a mild and effective technique for nitrate ester removal. In order to test this photochemical deprotection process (Scheme I), compounds **1**–**3** were synthesized[3] and irradiated.

Scheme I

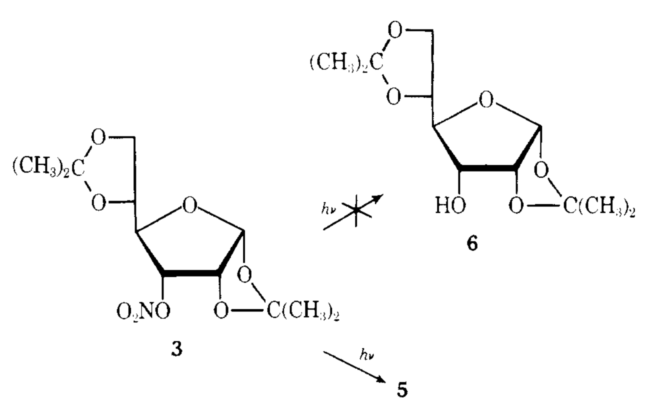
$$\mathrm{RONO_2} \xrightarrow{h\nu} \mathrm{RO\cdot}\ \ \cdot\mathrm{NO_2} \xrightarrow[\text{donor}]{\text{hydrogen}} \mathrm{ROH}$$

Photochemical reaction of each of the three nitrates **1**–**3** was conducted in the same manner. Corex-filtered irradiation of 1.0 g of material in 350 mL of 2-propanol under nitrogen with a 450-W Hanovia mercury lamp for 1 h resulted in complete disappearance of starting material and formation of a single photoproduct. Compound **1** quantitatively produced the corresponding alcohol[4] **4** and compound **2** gave its corresponding alcohol[5] **5** in 92% yield. Surprisingly, however, irradiation of **3** did not result in the expected product **6** but rather the C_3 inverted alcohol **5** (100% yield). Identical results were obtained when compounds **1**–**3** were irradiated in butyl ether.



1 **4** **2** **5**

Although photochemical N–O bond homolysis followed by hydrogen abstraction from the solvent (Scheme I) explained satisfactorily the reactions of **1** and **2**, conversion of **3** into **5** required further explanation. Since one of the four bonds to C_3 must have been broken during reaction, the possible fragmentation of each of these four bonds needed to be considered. The C_3–O cleavage consistent with the exclusive formation



3 **6** **5**

of **5** from **3** involved rearrangement of **3** into its epimeric nitrate ester **2** followed by further reaction of **2**. (Other processes which involve C–O bond breaking such as formation of a radical, cationic, or anionic center at C_3 could be excluded because reaction at this center with solvent would have produced products not observed.) The intermediacy of **2** was tested by irradiation of **3** to partial (27%) completion and analysis of the reaction mixture. Only compound **5** and the starting material (**3**) could be detected. Since **2** and **3** have comparable UV spectra and are consumed at comparable rates during photolysis, **2** should have been present in the reaction mixture if it were an intermediate in the formation of **5**.

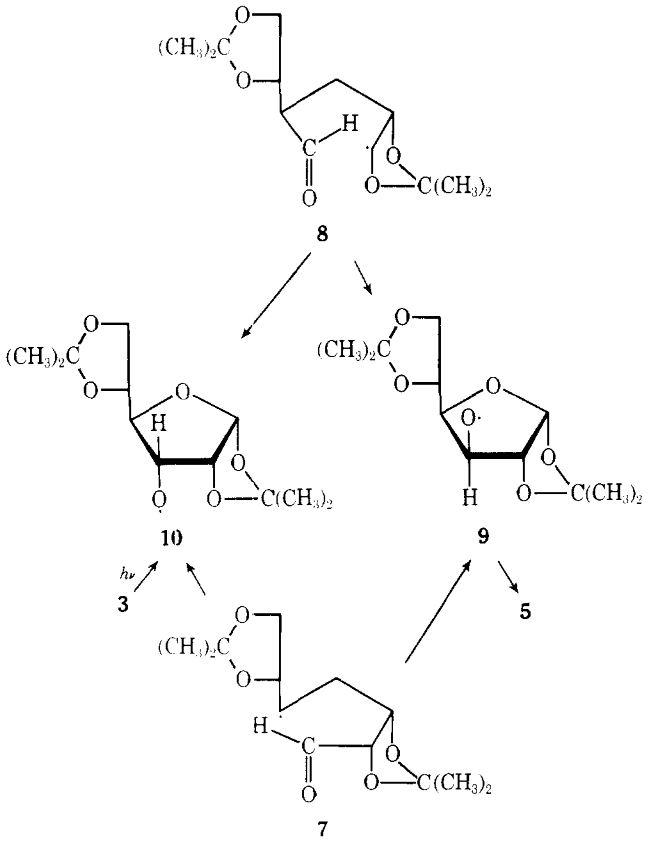
$$\mathbf{3} \not\longrightarrow \mathbf{2}$$

The possibility that inversion of configuration during photolysis of **3** resulted from the C_3–H bond being broken and re-formed was tested by irradiation of **3** in 2-propanol-d_8. The observed formation of **5** without deuterium incorporation at C_3 was not consistent with C_3–H bond fragmentation.

These results suggested that the inversion of configuration taking place during photolysis of **5** arose through a ring-open intermediate such as **7** or **8** (Scheme II). Ring opening of alkoxy radicals with neighboring methoxy groups and subsequent reclosure with inverted stereochemistry has been observed in reactions of steroids;[6] thus, analogy exists for the type of rearrangement proposed in Scheme II.[7] Ring opening to give **8** rather than **7** would be expected because the dipole–dipole repulsion between the C_2–O and C_3–O bonds should weaken the C_2–C_3 bond relative to the C_3–C_4 bond. Minimization of dipole–dipole interaction also would explain reclosure with inverted stereochemistry (i.e., formation exclusively of **9**). A further observation favoring C_2–C_3 cleavage is that C_3–C_4 fragmentation would allow inversion of configuration at C_4; however, no C_4 inverted product was formed.

Although all available information was consistent with a ring-open intermediate in the rearrangement of **3** to **5**, a more direct test of this proposed mechanism seemed desirable. An irradiation of **3** was conducted in the presence of octyl mercaptan in the hope of transferring a hydrogen atom to a ring-open intermediate; unfortunately, the mercaptan had no effect on the reaction. A second approach to testing this process consisted of attempting to generate the radical **10** by a nonphotochemical process and observing its reaction. Reaction of alcohols with lead tetraacetate is an effective technique for generating alkoxy radicals;[8] consequently, **6** was treated with lead tetraacetate in refluxing cyclohexane[9] and found to rearrange quantitatively to **5**. Thus, the reaction of **6** with lead tetraacetate and the photolyses of **3** under the various conditions described above seem best explained by the reaction pathway outlined in Scheme II.

Scheme II



$$\mathbf{6} \xrightarrow[\substack{C_6H_{12}\\ \text{reflux}}]{Pb(OAc)_4} \mathbf{5}$$

Finally, photolysis of nitrate esters appears to have promise as a mild technique for deprotecting alcohols, although further investigations are necessary to determine precisely which types of compounds will experience rearrangement.

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Nucleophilic Substitution between a Gaseous Alkyl Halide and a Solid Salt, Promoted by Phase-Transfer Catalysts

Summary: By passing a gaseous alkyl halide over a catalytic column composed of a salt, a solid support, and a phase-transfer catalyst, the substitution product is obtained. The phase-transfer catalyst can be either free or immobilized on a silica matrix; in this way syntheses of alkyl iodides and esters are possible.

Sir: Normally nucleophilic substitution reactions between an alkyl halide and a nucleophilic source, such a metallic salt, in a solid state and without solvents do not take place. Even when the temperature is increased and the alkyl halide is gaseous, there is no reaction between it and the solid salt. It is only when the latter is in a molten condition that the reaction proceeds rapidly.

Experiments in this field were carried out by Packham and