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

$$3 \nrightarrow 2$$

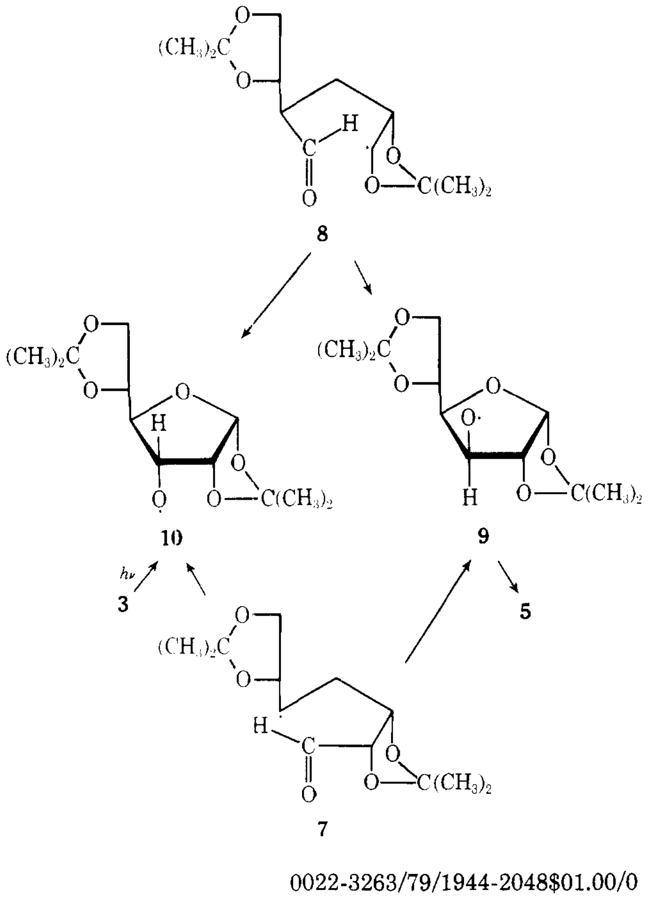
comparable UV spectra and are consumed at comparable rates during photolysis, **2** should have been present in the reaction mixture if it were an intermediate in the formation of **5**.

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



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

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

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Figure 1.

Rackley,[1] who passed a simple alkyl halide over a molten layer of an alkaline salt; though the presence of eutectic mixtures considerably lowered the melting point of the mass, the temperature remained fairly high. Therefore numerous byproducts were also obtained.

We have now found that such reactions can be easily carried out at a much lower temperature if they are effected in the presence of a phase-transfer catalyst.[2] When a gaseous alkyl halide is passed over a solid catalytic bed composed of a salt, a PT catalyst, and a solid support, the substitution reaction takes place, as follows:

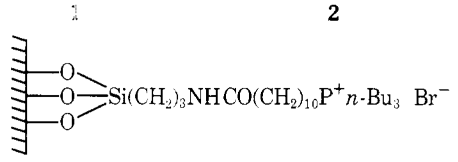
$$RX_{gas} + M^+Y^-_{sol} \xrightarrow{cat.} RY_{gas} + M^+X^-_{sol} \qquad (1)$$

In the present case the catalytic bed is set up in a column 30 cm long and 2 cm in diameter and heated to 150 °C in an oil bath (Figure 1). The alkyl halide is introduced into the column either at atmospheric or reduced pressure, according to its boiling point. Both the substrate and the product must be gaseous in the reaction medium.

The PT catalyst can be phosphonium salts either free (**1**, **2**) or immobilized on silica gel[3] (**3**, 1.10 mequiv of P^+/g). It is

$n\text{-}Bu_4P^+\ I^-$ **1**

$n\text{-}C_{16}H_{33}P^+n\text{-}Bu_3\ Br^-$ **2**



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necessary to use phosphonium salts as they can be kept at 150 °C for several days without appreciable decomposition, while ammonium salts decompose at this temperature.[4]

The catalytic beds were prepared by dissolving 0.052 mol of salts (KI, 8.63 g; Na butyrate, 5.72 g) and 0.0052 mol of catalyst (**1**, 2.01 g; **2**, 2.64 g) in a mixture of methanol and water; the solid support silica gel (to a total of 20.0 g) was added and the solvents were removed; then the solid mass was placed in a stove at 120 °C for 2 h.

Passing 1-chlorobutane (0.026 mol, 2.41 g) through this catalytic bed (placed in the column at 150 °C and filled by KI and **1**) with the aid of a peristaltic pump for a period of 5 min, 1-iodobutane was obtained at the exit by condensing the gaseous products. ^1H NMR analysis showed a conversion of 45% (no byproducts are observed in GLC). To improve the conversion the collected liquid products were recycled in the same column several times in the same conditions: after the third passage 75% and after the fifth 91% of conversion to 1-iodobutane (4.40 g) was obtained.

In the same way, starting from 1-bromooctane (0.026 mol, 5.02 g) and working at 20 torr with the column filled by KI and **2**, 1-iodooctane was obtained with a 78% (first passage) and 92% conversion (5.95 g) at the third passage.

When the catalytic bed was composed of sodium butyrate and **1** and ethyl bromide (0.026 mol, 2.83 g) was forced to pass though, always for 5 min at 150 °C, ethyl butyrate was obtained with a 55% (first passage), an 87% (third passage), and a 98% conversion (2.90 g, fifth passage).

Even when the phosphonium salt is immobilized on a polymeric matrix this type of catalysis is possible; the solid support is unnecessary for the preparation of the latter catalytic bed (indeed it would be counterproductive); it is sufficient to dissolve the salt in water, add the immobilized catalyst, and remove the water completely.

Passing 1-bromobutane (0.026 mol, 3.56 g) over the catalytic bed composed by KI (0.056 mol, 8.63 g) and **3** (0.0056 mol equiv, 4.73 g) in the same conditions stated before, 1-iodobutane (4.20 g) was obtained with a 67% conversion in the first passage.

According to eq 1, when an halide reacts with the salt placed in the column, the salt M^+X^- is deposited there in its place. It is thus possible to carry out another nucleophilic substitution on the same catalytic bed, after the salt M^+Y^- is exhausted:

$$R'X'_{gas} + M^+X^-_{sol} \xrightarrow{cat.} R'X_{gas} + M^+X'^-_{sol} \qquad (2)$$

In this way two successive reactions can be carried out on the same catalytic bed. For example NaI was deposited during the synthesis of methyl butyrate when methyl iodide (0.026 mol, 3.69 g) was passed over the catalytic bed composed by sodium butyrate and **1** (2.70 g, 80% conversion after the first passage). After about 0.15 mol of methyl iodide had been passed, almost all the primary salt was transformed into NaI; then, passing 1-bromobutane (0.026 mol, 3.56 g) for a period of 5 min at 150 °C, 1-iodobutane (4.60 g) was rapidly obtained with a 95% conversion, in the first passage.

As these reactions do not take place in the gaseous phase, they must take place in the liquid one, constituted by the molten catalyst, and into which the gaseous alkyl halide must diffuse. The liquid phase is finely dispersed and adsorbed along the porous solid support and therefore has an increased surface extension. However, it seems that an effective liquid phase is not necessary, since even immobilized catalysts promote the substitution reaction.

Two equations should be considered. The first is the nucleophilic displacement of the halide by the molten catalyst,

$$RX + Q^+Y^- \rightleftharpoons RY + Q^+X^- \qquad (3)$$

which is controlled by the diffusion of the gaseous halide in the liquid phase. The second is the exchange of anions between the catalyst and the salt:

$$Q^+X^- + M^+Y^- \rightleftharpoons Q^+Y^- + M^+X^- \qquad (4)$$

This latter equilibrium is controlled by the melting point of the two catalytic species Q^+Y^- and Q^+X^-, or better, by the formation of eutectic mixtures from all the four salts involved.

This is different from the liquid–liquid PTC in which eq 4 is controlled by the solubility of the two catalytic species in the organic and aqueous phases.

Supplementary Material Available: Experimental Section describing the synthesis of 1-iodobutane from 1-chlorobutane (1 page). Ordering information is given on any current masthead page.

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