coupling constant supports this conclusion. In $CDCl_3$ solution the situation is qualitatively similar, but the preference for *gauche* is much less pronounced. We thus conclude that the 1,4-*gauche* CH⋯O interaction is attractive, and competitive with the chloroform-ether interaction, when CH is made sufficiently acidic by the adjacent ether oxygen. Also the chemical shift data led to this conclusion. The dipole moment measured in benzene solution is 1.57 D (and 1.35 D for 1,3-dimethoxy-2,2-dimethylpropane) and this is significantly lower than calculated for randomly oriented ether groups (1.3 D × $\sqrt{2}$ = 1.8 D) or for the *aa*-conformer (2.6 D), and so supports a general *gauche* preference. The even lower dipole moment of the 2,2-dimethyl derivative shows that there is no competition for the ether oxygen from the non-acidic methyl protons.

Experimental. Dipropyl ether was bought from Fluka and was used without purification. The methyl alkyl ethers were prepared [12] by gently heating the corresponding alcohol with dimethyl sulfate and distilling until the vapour temperature reached 100 °C. The distillate was passed through an alumina column and redistilled from sodium metal. Methyl propyl ether, b.p. 39 − 40 °C; methyl butyl ether, b.p. 70 − 71 °C; methyl isobutyl ether, b.p. 59 − 60 °C.

1,3-Dimethoxy-2,2-dimethylpropane was prepared [13] from neopentyl glycol by reaction with sodium hydride and methyl iodide in dry tetrahydrofuran and the product purified on an alumina column.

Dimethoxypropane [14] was prepared by the action of dimethyl sulfate on the dry disodium salt of trimethylene glycol (from sodium methoxide and trimethylene glycol in methanol). The distillate was twice redistilled from solid sodium hydroxide, passed through an alumina column and finally distilled from sodium hydride; b.p. 106 − 107 °C.

No impurity signals were apparent in the NMR spectra of the ethers so prepared.

The NMR spectra were recorded on a Varian HA 100 instrument for solutions containing about 7 % of the ether and TMS as internal reference. The dipole moments were determined as described previously.[15]

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The Use of Tetrabutylammonium Azide in the Curtius Rearrangement

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The conversion of a carboxylic acid chloride to the corresponding azide is traditionally carried out with sodium azide.[1] The insolubility of the latter in common organic media makes it desirable to use a water-containing solvent mixture, *e.g.*, with aromatic acid chlorides. With lower aliphatic acid chlorides, their sensitivity to hydrolysis precludes the use of protic solvents, and heterogeneous conditions have to be accepted, leading to irreproducible results.

The use of hydrazoic acid and pyridine is described in a recent communication.[2] Acyl azides can thus be prepared under mild and homogeneous conditions. The same is the case when tetramethylguanidinium azide is used.[3] However, the latter two methods require the

Table 1. Preparation and rearrangement of acyl azides from tetrabutylammonium azide.

Starting chloride	Solvent [a]	Per cent N_2 evolved	Product isocyanate, b.p. (°C) found; lit.[b]	Per cent yield of aniline derivative	Aniline derivative m.p. (°C) found; lit.[b]
Acetyl	B	84	Methyl, 38; 40	52	150; 149–150
Propionyl	B	93	Ethyl, 61.5; 59.8	61	98–99; 100
Butyryl	T	93	Propyl, 88–90; 88	73	115.5–116.5; 116–116.5 [c]
Isovaleryl	B	90	Isobutyl, 102; 104–106	86	151–152; 151–152
Pivalyl	T	97	t-Butyl, 85.5; 84.6	60	167.5–168.5; 167–168
4-Chlorobutyryl	T	87	3-Chloropropyl, 60–61 at 2.7 kPa; 54.6–54.8 at 2.1 kPa	78	123–124; 127
Benzoyl	T	96	Phenyl, 158–162; 55 at 1.7 kPa	89	238–239; 237–237.5

[a] B, benzene; T, toluene. [b] Literature values from *Beilstein* unless otherwise indicated. [c] See ref. 8.

handling of hydrazoic acid with its concomitant hazards.

The present paper describes a method of azide synthesis, in which the azide ion is readily extracted as an ion-pair with tetrabutylammonium ion from an aqueous solution into an organic phase.

Tetrabutylammonium azide has been obtained in pure, crystalline form after extraction into methylene chloride, followed by evaporation of the solvent. This azide has earlier been prepared from hydrazoic acid and tetrabutylammonium hydroxide.[4-6] The azide, which apparently can be safely handled in dry form, is soluble in a number of organic solvents. Metathesis with carboxylic acid chlorides can thus be carried out in a one-phase system. The resulting acyl azides can be directly used in subsequent reactions.

In the present work, a number of acyl azides have been prepared and made to rearrange to isocyanates by heating. The reactions were followed by the nitrogen evolution. The isocyanates formed were characterized by conversion to substituted ureas with aniline.

It is possible to perform reactions with the isocyanates in the same solution that was used in the Curtius rearrangement. Final separation from the tetrabutylammonium chloride should ordinarily cause no problems, since the salt is readily removed from organic solvents by water.

Results obtained with different acyl chlorides are summarized in Table 1.

Experimental. Tetrabutylammonium azide. A solution containing 0.2 mol of tetrabutyl-ammonium hydroxide was prepared by addition of 50 ml of 10 M sodium hydroxide solution (an excess) to 67.9 g (0.2 mol) of tetrabutylammonium hydrogen sulphate in 100 ml of water. A solution of 26 g (0.4 mol) of sodium azide in 50 ml of water was added and tetrabutylammonium azide extracted with 100 ml of dichloromethane. It is important to have an excess of sodium hydroxide in order to avoid extraction of free hydrazoic acid, which might make the subsequent operations very dangerous. The organic layer (upper phase), 170 ml, was separated off and the aqueous phase again extracted with 100 ml of dichloromethane (lower phase). The combined organic phases were evaporated *in vacuo* at 40 °C to yield 59.8 g (theor. 56.9 g) of crude tetrabutylammonium azide as a colourless oil. Residual water was removed by azeotropic distillation with benzene or toluene. The solutions thus obtained were used directly in the following step. If so desired, the dry tetrabutylammonium azide can be obtained in quantitative yield as a crystalline, hygroscopic solid by evaporation of the solvent *in vacuo*. Recrystallization from toluene gives colourless crystals, m.p. 80 °C, lit.[6] 80 °C (decomp.).

Curtius rearrangement. A dry solution of 0.2 mol of tetrabutylammonium azide (the above batch) in 150 ml of benzene or toluene (see Table 1) was placed in a round-bottomed flask equipped with a reflux condenser, a thermometer, a stirrer and a dropping funnel. To this solution the equivalent amount (0.2 mol) of freshly distilled acyl chloride in 150 ml

of benzene or toluene was added in portions. The temperature was kept below 25 °C by cooling in ice water. The mixture was left for 3 – 4 h and then heated, a gas burette being attached to the top of the reflux condenser. Nitrogen evolution started at 50 – 90 °C. The gas evolution was allowed to proceed at a brisk rate by gradual heating, giving a total reaction time of less than 4 h. The isocyanate was separated from the solvent by distillation through a 30 cm stainless steel spiral column having 5 mm internal diameter. Because of the instability of isocyanates, yields were variable but usually better than 50 %.

To obtain a better determination of the yields, the Curtius rearrangement was repeated (on a 7 mmol scale). After the nitrogen evolution had ceased, a slight excess of aniline was added to the reaction mixture. The resulting N-alkyl-N'-phenyl urea was freed from tetrabutylammonium chloride by washing the solution with water. The organic solvent was evaporated and the resulting product recrystallized from aqueous ethanol. The yields of the urea derivatives obtained are given in Table 1. The reaction with aniline is assumed to be quantitative,[7] and the recrystallization losses are small. The identity was further verified by ^{1}H NMR.

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Reinvestigation of the Synthesis of Thiete 1,1-Dioxide

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The four-membered cyclic unsaturated title compound was needed as a synthetic intermediate in our work. Dittmer and Christy [1,2] first prepared it as indicated in Fig. 1. Since
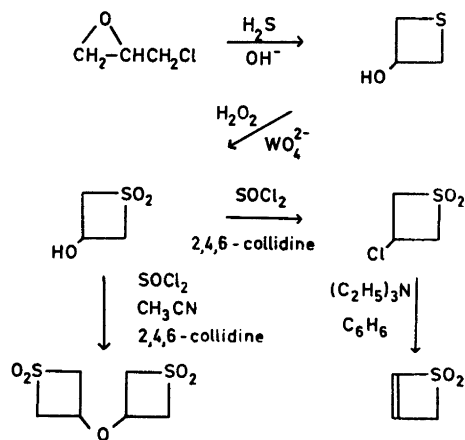

Fig. 1. Synthetic route to thiete 1,1-dioxide and bis-(3-thietanyl 1,1-dioxide) ether.

the yield in the first step was only 39 %, and since the second step involved a reportedly [2] hazardous evaporation of peracetic acid, an alternative synthetic route was later described.[3] This starts with a 2 + 2 cycloaddition of sulfene to N,N-dimethylvinylamine. The latter compound is very unstable, requiring low temperature and oxygen-free conditions, and we did not deem a large-scale preparation attractive.

Upon reinvestigation of the original procedure, we found that the first step is much more conveniently carried out in potassium hydroxide solution than with barium hydroxide.[1] The reaction of epichlorohydrin with hydrogen sulfide in basic solution was first described by Sjöberg.[4] He obtained 30 % yield with potassium hydroxide, but a much higher yield, 65 %, is actually secured by continuous extraction of the aqueous phase with ether.

The second step, oxidation of 3-thietanol to the sulfone, can advantageously be carried out with 30 % aqueous hydrogen peroxide and a catalytic amount of sodium tungstate [5] instead of the usual mixture of aqueous hydrogen peroxide and acetic acid.[1]