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Electrophilic Additions and Substitutions of *tert*-Butyl Hypochlorite Catalyzed by Boron Trifluoride[1]

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In nonpolar solvents with light or radical initiators, *tert*-butyl hypochlorite reacts with olefins to give allylic chlorides in good yield by a radical chain process.[2] On the other hand, Anbar and Ginsberg, in their comprehensive review,[3] report that, in polar solvents, addition occurs to yield β-chloro ethers *via* electrophilic addition where R′ is either *tert*-butyl or, in an alcohol solvent, the corresponding alcohol residue. Since we had need of such products for another study,[4] and since yields and procedures were ill-defined in the original papers cited by Anbar, we have reexamined this polar addition, and find that the success of the reaction depends markedly upon reaction conditions but proceeds particularly smoothly simply by adding the hypochlorite to cold olefin–alcohol mixture containing a few drops of boron trifluoride etherate. Yields are 50–90% and, of particular interest, β-chloro-*tert*-alkyl ethers can be produced which are difficulty accessible by other means. Typical results are shown in Table I, and we assume that reaction occurs *via* a typical "chloronium ion" intermediate which then reacts with solvent as the predominant nucleophile. Although the preparation appears general for simple olefins, it fails with negatively substituted olefins such as 1,1- and *cis*-1,2-dichloro- and trichloroethylene.

$$t\text{-BuOCl} + CH_2{=}CHR \rightarrow ClCH_2CH(OR')R$$

We were also unable to observe any cyclized product on attempting to prepare the hypochlorite from 4-penten-1-ol *in situ* and then carrying out the addition, although others have reported accomplishing the cyclization *via* a radical path.[5]

Anbar[3] also reports a few examples of acid-catalyzed electrophilic aromatic substitution by *tert*-butyl hypochlorite, and such reactions have occasionally been noted as complications in attempted radical chlorination of alkylbenzenes with strong electron-supplying groups and in the reactions of complex hypochlorites containing reactive aromatic nuclei.[4] We find that the *tert*-butyl hypochlorite–boron trifluoride technique leads to smooth chlorination of benzene, chlorobenzene, and toluene at room temperature, although the reaction fails with more negatively substituted aromatics. With toluene we obtain an isomer distribution of 70.2% ortho and 29.8% para and, in competition, toluene is 21 times as reactive as benzene. For Cl_2 in acetic acid the isomer distribution is reported as 59.8% ortho, 0.5% meta, and 39.7% para with toluene 344 times as reactive as benzene,[6] while with hypochlorous acid in water the isomer distribution is 74.6% ortho, 2.2% meta, and 23.2% para with a total reactivity 60 times that of benzene.[7] Our results are much closer to the latter, and indicate that the electrophilic species is indeed a *tert*-butyl hypochlorite–boron trifluoride complex, rather than traces of adventitious Cl_2 which might be formed during the reaction. With *tert*-butylbenzene we obtain a mixture of 53% ortho and 47% *p*-chloro substitution.

In summary, our results show that a variety of electrophilic addition and substitution reactions of *tert*-butyl hypochlorite (and presumably other alkyl hypochlorites) can be carried out in good yield under very mild conditions using small amounts of boron trifluoride catalyst. The reaction provides a simple, efficient synthesis of β-chloro ethers and a convenient laboratory alternative to gaseous Cl_2 for the chlorination of suitable aromatic nuclei.

Experimental Section

β-Chloro Ethers. The preparation of 2-chlorocyclohexyl isopropyl ether is typical. Anhydrous isopropyl alcohol (0.1 mol), cyclohexene (0.1 mol), and a few drops of boron trifluoride etherate were placed in a 25-ml flask cooled in ice water. *tert*-Butyl hypochlorite (0.03 mol) was added dropwise with stirring. Each drop apparently reacted immediately. The solvent was removed *in vacuo* and the product was distilled, yield 2.3 g (43.2%), bp 48° (0.1 mm). Analysis and nmr spectra were consistent with the assigned structure and vpc indicated a single isomer, assumed to have the trans structure. Other reactions were carried out similarly, using equimolar quantities of alcohol and olefin, except that addition to isobutylene was made at −78°. Yields were determined either by vpc or actual isolation as indicated in Table I.

Table I
Preparation of β-Chloro Ethers

Olefin	Registry no.	Product	Registry no.	Yield, % Vpc	Yield, % Isolated
Cyclohexene	110-83-8	*trans*-2-Chlorocyclohexyl *tert*-butyl ether	51286-79-4	49	49
Cyclohexene		*trans*-2-Chlorocyclohexyl isopropyl ether	51286-80-7	57	43
Cyclohexene		*trans*-2-Chlorocyclohexyl *n*-propyl ether	51286-81-8	96	66
Isobutylene	115-11-7	Chloro-*tert*-butyl *n*-propyl ether	51286-82-9	67	

Aromatic substitution reactions were carried out by adding hypochlorite at or below room temperature to an excess of the appropriate aromatic (or mixture) in the presence of a small amount of boron trifluoride etherate but no added solvent. The yellow color of the hypochlorite disappeared within 0.5 hr, and total yields (essentially quantitative) and product distributions were determined by vpc using known standards. The spread of analytical results indicated that the isomer distributions reported are reliable to ±1–2%.

Registry No.—*tert*-butyl hypochlorite, 507-40-4; boron trifluoride, 7637-07-2.

References and Notes

(1) Taken from the Ph.D. Thesis of Roger T. Clark, University of Utah, 1973. Support of this work by a grant from the National Science Foundation is gratefully acknowledged.
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Molecular Rearrangements in the Course of Ritter Reactions

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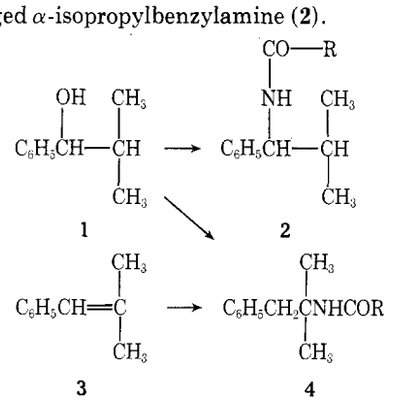
It is well known that the Ritter reaction occurs *via* ionic intermediates and that molecular rearrangements take place if the initial carbonium ion intermediate can isomerize to a more stable one.[2] Thus Boltze and Mühlenbein[3] reported that α-isopropylbenzyl alcohol (**1**) reacts with hydrogen cyanide or with nitriles under acidic conditions to yield amides of α,α-dimethylphenethylamine (**4**). On the other hand, this seems to contradict the report by Christol, *et al.*,[4] that Ritter reactions of **1** form amides of the unrearranged α-isopropylbenzylamine (**2**).



a, R = CH_3
b, R = C_6H_5

A check of the reaction conditions which were used by these two groups showed that a reasonable cause for this discrepancy could have been the different order of addition of reagents used, since this in turn could have easily changed the type of mechanistic factor which controlled the reactions. Thus, Boltze and Mühlenbein first mixed the carbinol and the acids, and only later added the nitrile, whereas Christol and coworkers first mixed the carbinol with the nitrile, and added the sulfuric acid last. In the first case, the initially formed carbonium ion may therefore have had ample time to rearrange into a more stable structure before the nitrile was added (*e.g.*, thermodynamic control of reaction), while in the second case the nitrile could trap the carbonium ions as they were being formed (*e.g.*, kinetic control). This would also explain Christol's additional observation that, while the Ritter reaction of **1** yielded **2**, the same reaction with the styrene derivative **3** only yielded **4**.

To check our rationalization, we only changed the order of addition of reagents when **1** was allowed to react with nitriles in a mixture of sulfuric and acetic acid under otherwise identical conditions. As was expected, **2** was obtained when sulfuric acid was the last reagent which was added, while **4** was obtained when the nitrile was added last.[5]

Experimental Section

Melting points were determined in capillaries and are uncorrected; nmr spectra were recorded on a Varian Associates A-60 spectrometer with TMS as internal standard.

α-Isopropylbenzyl Alcohol (1). To a refluxing suspension of 13 g (0.34 mol) of lithium aluminium hydride in 300 ml of tetrahydrofuran was added 100 g (0.675 mol) of isobutyrophenone (Aldrich) in 200 ml of tetrahydrofuran. After 2 hr of additional refluxing, the reaction mixture was cooled to room temperature and treated with 15 ml of water, 15 ml of 15% aqueous sodium hydroxide, and 39 ml of water. The suspension was filtered, the filter residue was washed thoroughly with 200 ml of tetrahydrofuran, and the solvent of the combined filtrates was evaporated under reduced pressure to yield 84.9 g of crude **1**, which was purified by fractionation over a Vigreux column and gave 73.9 g (0.526 mol, 78% of theory) of **1**, bp 77–78° (0.3 mm).

***N*-(α,α-Dimethylphenethyl)acetamide (4a).** To a solution of 6.0 g (0.04 mol) of compound **1** in 6.0 ml of glacial acetic acid and 3.3 ml of 95% sulfuric acid was added dropwise 1.9 g (0.046 mol) of acetonitrile at 70°, and the mixture was kept for an additional 1 hr at this same temperature. Then it was added to enough crushed ice to keep the resulting solution at room temperature, treated with 14 ml of 25% aqueous sodium hydroxide, returned just to acidic by addition of 15% aqueous sulfuric acid, and extracted in two steps with 150 ml of methylene chloride. The combined extracts were washed with 3 × 50 ml of water and dried over sodium sulfate and the solvent was evaporated under reduced pressure to yield 7.1 g of an oil, which crystallized in cyclohexane to give 2.7 g (0.014 mol, 35% of theory) of **4a**: mp 89–90° (lit.[3] mp 91–92°); nmr ($CDCl_3$) 2 CH_3 at 1.29 (s), CH_3 at 1.85 (s), CH_2 at 3.02 (s), C_6H_5 at 7.19 ppm (complex).

***N*-(α,α-Dimethylphenethyl)benzamide (4b).** By the method described for the preparation of **4a**, but using 3.3 g (0.032 mol) of benzonitrile instead of the acetonitrile, the crude product was 6.4 g of crystalline material which was purified by recrystallization in 95% ethanol: mp 109–110°; nmr ($CDCl_3$) 2 CH_3 at 1.43 (s), CH_2 at 3.14 (s), 10 aromatic at 7.1–7.8 ppm (complex).

Anal. Calcd for $C_{17}H_{19}NO$: C, 80.60; H, 7.56; N, 5.53. Found: C, 80.95; H, 7.33; N, 5.57.

***N*-(α-Isopropylbenzyl)acetamide (2a).** To a solution of 6.0 g (0.04 mol) of **1** and 1.9 g (0.046 mol) of acetonitrile in 6.0 ml of glacial acetic acid was added 3.3 ml of 95% sulfuric acid at 70°. After the previously described work-up, which yielded 6.6 g of crude product, a recrystallization in 2-propanol gave 2.6 g (0.0135 mol, 34% of theory) of **2a**: mp 114–116°; nmr ($CDCl_3$) CH_3 at 0.78 (d), CH_3 at 0.95 (d), CH_3 at 1.9 (s), CH at 1.9 (heptet), CH at 4.7 (broad triplet), C_6H_5 at 7.2 ppm (s).

Anal. Calcd for $C_{12}H_{17}NO$: C, 75.40; H, 8.96; N, 7.32. Found: C, 75.60; H, 8.56; N, 7.37.

***N*-(α-Isopropylbenzyl)benzamide (2b).** By the method described for the preparation of **2a**, but using 3.3 g (0.032 mol) of benzonitrile instead of acetonitrile, the crude product was 6.2 g of crystalline material, which was purified by recrystallization in ethanol: mp 139–140° (lit.[4] mp 141°); nmr ($CDCl_3$) CH_3 at 0.87 (d), CH_3 at 1.02 (d), CH at 2.23 (heptet), CH at 5.01 (broad triplet), 10 aromatic at 7.4–7.9 ppm (complex).

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Registry No.—**1**, 611-69-8; **2a**, 33617-85-5; **2b**, 51310-27-1; **4a**, 5531-33-9; **4b**, 51310-28-2; isobutyrophenone, 611-70-1.

References and Notes

(1) To whom inquiries should be directed to Dyestuffs & Chemicals Division, CIBA-GEIGY Corp., P.O. Box 11422, Greensboro, N. C. 27409.
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N-Acyllactam Rearrangements. The Fate of the Carboxyl Carbon and the Synthesis of 2-*tert*-Butyl-1-pyrroline

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The rearrangement of *N*-acyllactams to 2-substituted cyclic imines has recently been investigated in our labora-