A Novel Synthesis of Perhalogenated Alkenes[1]

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Introduction

Many methods have been developed for the preparation of fluorinated alkenes due to their importance as reactive intermediates for the synthesis of a broad range of fluorochemicals and materials.[3] The most common laboratory method is the dehalogenation of a vicinal dihalide (usually Cl, Br) with zinc in a polar solvent. Frequently, the available methods for alkene synthesis are difficult to apply to a halogenated alkane having multiple elimination pathways and/or bearing a reactive substituent.

In the course of other research on the synthesis of (fluoroalkyl)silanes, we unexpectedly found that tris(diethylamino)phosphine is an effective dehalogenating reagent. It exhibits excellent selectivity for vicinal dehalogenation of a variety of fluoroalkanes and provides a route to alkenes that are difficult to obtain by other methods. Several examples of this useful reactivity are presented.

Experimental Section

^{19}F NMR spectra (188.3 MHz) were recorded in $CDCl_3$ with $CFCl_3$ as an internal reference. IR spectra were recorded in the gas phase using a 10-cm cell. Products were purified by vacuum distillation through a series of cold traps. Boiling points were measured by Siwoloboff's[4] method and are uncorrected.

Tris(diethylamino)phosphine (9). Mark's preparation of the analog tris(dimethylamino)phosphine[5] was followed with these minor modifications: the solvent pentane was used instead of ether, as it made the diethylammonium chloride byproduct easier to filter; the quantity of solvent had to be doubled to permit stirring; and the reaction was worked up as soon as the addition of Et_2NH to PCl_3 was completed. Starting with 78 g (0.57 mol) of PCl_3 and 256 g (3.5 mol) Et_2NH, **9** (110 g, 78% yield) was obtained, after distillation.

General Procedure. Into a 1 M solution of starting compound in benzonitrile was added 1 mol equiv of **9** dropwise under magnetic stirring. Cooling was provided by an ice–salt bath. Upon the completion of the addition (10–30 min) the reaction vessel was cooled to −196 °C, connected to the vacuum line, evacuated to 10^{-3} mmHg, and then allowed to warm to 22 °C while the vapors were fractionated through a series of cold traps. The reactions were conducted on a 5–15 mmol scale.

3-Chloro-1,1,2,3,3-pentafluoroprop-1-ene[6] (4). $CF_2BrCFBrCF_2Cl$ (1.27 g) and **9** in benzonitrile gave $CF_2{=}CFCF_2Cl$ (**4**) (0.60 g, 90%) in a −196 °C trap. IR: 1781 cm^{-1}. ^{19}F NMR δ −57.4 (2 F, d-d-d, J = 30, 18.8, 6.0 Hz), −93.7 (1 F, m, J = 116.5, 37.7, 18.8 Hz), −104.6 (1 F, M, J = 116.5, 53, 30 Hz), −184.2 (1 F, m, J = 53, 37.7, 6.0 Hz).

1-Bromo-2,3,3,4,4-pentafluorocyclobutene[7] (5). c-$CF_2CF_2CFBrCBr_2$ (1.95 g, PCR, Inc.) and **9** in benzonitrile gave c-$CF_2CF_2CF{=}CBr$ (**5**) (0.40 g, 41%) collected in a −196 °C trap. IR: 1707 cm^{-1}. ^{19}F NMR: (A_2B_2C spin system) δ −108.9 (1 F, t-t, J = 16.5, 6 Hz), −118.0 (2 F, m), −118.4 (2 F, m). Vapor density: found 228.0, calcd 223.0.

Table I. Dehalogenation Reactions Using Tris(diethylamino)phosphine

starting compd	structure	product no.	product yield (%)
$CF_2ClCFClBr$[a]	$CF_2{=}CFCl$	1	80
$CF_2BrCFBrCl$[b]	$CF_2{=}CFCl$	1	78
$CF_2ClCFClI$[c]	$CF_2{=}CFCl$	1	92
$CFCl_2CFCl_2$[d]	$CFCl{=}CFCl$[e]	2	90
$CF_3CF_2CH_2Br$[f]	$CF_3CF{=}CH_2$	3	60
$CF_2ClCFClCF_2Cl$[c]	$CF_2{=}CFCF_2Cl$	4	76, 0[g]
$CF_2BrCFBrCF_2Cl$[h]	$CF_2{=}CFCF_2Cl$	4	86
c-$CF_2CFBrCBr_2CF_2$[c]	c-$CF_2CF{=}CBrCF_2$	5	41, 34[g]
$CF_2ClCFClCF_2CF_2I$[c]	$CF_2{=}CFCF_2CF_2I$	6	70
$CF_2ClCFClCFClCF_2Cl$[c,i]	$CF_2ClCF{=}CFCF_2Cl$	7	95
$CF_2ClCFClCCl_2CF_2Cl$[i]	$CF_2ClCF{=}CClCF_2Cl$	8	56

[a] From $CF_2{=}CFBr$ and Cl_2. [b] From **1** and Br_2. [c] Commercial product. [d] From $CFCl{=}CFCl$ and Cl_2. [e] *E*:*Z* ratio = 1:1. [f] Cf. ref 10. [g] With $((CH_3)_2N)_3P$. [h] From **4** and Br_2. [i] *E*:*Z* ratio, cf. Experimental Section.

4-Iodo-1,1,2,3,3,4,4-heptafluorobut-1-ene (6). $CF_2ClCFClCF_2CF_2I$ (2.0 g, PCR, Inc.) and **9** in benzonitrile gave $CF_2{=}CFCF_2CF_2I$ (**6**) (1.2 g) collected at −100 °C. Bp: 75–77 °C (lit.[8] bp 74–76 °C). IR: 1786 cm^{-1}. ^{19}F NMR: δ −62.2 (2 F, m), −88.1 (1 F, m), −105 (1 F, m), −112.6 (2 F, m), −188 (1 F, m). Coupling constants of the vinylic fluorines: cis 39 Hz, trans 118 Hz, *gem* 50 Hz. MS: 308 (M^+), 181 ($M - I)^+$.

1,4-Dichloro-1,1,2,3,4,4-hexafluorobut-2-ene (7). $CF_2ClCFClCFClCF_2Cl$ (1.4 g) and **9** in benzonitrile gave **7** (1.0 g, 95%) in nearly quantitative yield. Bp 65–68 °C (lit.[9] bp 64–66 °C). According to NMR integration the *E* and *Z* isomers were in a 4:1 ratio. IR: 1710, 1708 cm^{-1} (lit.[10] 5.84μ = 1712 cm^{-1}). ^{19}F NMR (*E* isomer) δ −58.5 (2 F, m), −153.6 (1 F, m); (*Z* isomer) δ −55.7 (2 F, m), −138.1 (1 F, m). MS: 232 (M^+), 213 ($M - F^+$), 197 ($M - Cl^+$).

1,2,4-Trichloro-1,1,3,4,4-pentafluorobut-2-ene (8). From $CF_2ClCFClCCl_2CF_2Cl$[11] (1.8 g) and **9** was obtained **8** as the only product by NMR of the reaction mixture, but purification from benzonitrile proved difficult. The isolated yield of pure **8** (1.1 g) was 56%. Bp: 105–107 °C. *E* to *Z* isomer ratio was, as for **3**, 4:1 by NMR integration. IR: 1726, 1660 cm^{-1}. ^{19}F NMR (*E* isomer): δ −52.0 (2 F, d, J = 33 Hz), −56.8 (2 F, d, J = 9 Hz), −109.3 (1 F, t-t, J = 33, 9 Hz); (*Z* isomer) δ −48.9 (2 F, t-d, J = 20, 6 Hz), −54.9 (2 F, t-d, J = 12, 20 Hz), −103.6 (1 F, m, J = 6 Hz). MS: 230 ($M - F^+$), 214 ($M - Cl^+$).

2,3,3,3-Tetrafluoroprop-1-ene[12] (3). $CF_3CF_2CH_2Br$[13] (1.0 g) and **9** were stirred in benzonitrile at 22 °C for 1 d. Conversion of the starting material was 50%. After addition of 1 further mol equiv of **9**, the bromide was consumed in 5 d. In a liquid nitrogen trap, **3** (0.34 g) was obtained in 60% yield. Vapor density: found 113, calcd 114. IR: 1693 cm^{-1}. ^{19}F NMR: δ −73.7 (3 F, d, J = 10 Hz), −124.3 (1 F, m). ^1H NMR: δ_{TMS} 5.2–5.4 (m). MS: 114 (M^+).

The well-known products **1** and **2** were also obtained while studying the reactivity of **9** with compounds carrying different halogens: cf. Table I and Discussion.

Results and Discussion

Tris(diethylamino)phosphine (**9**) has been found to be efficient and selective in dehalogenation reactions, as

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shown by the synthesis of 6, 7, and the novel 8 as pure substances. No other products were detected by NMR analysis before fractionation. Iodobutene 6 had previously been obtained by Knunjants and Pervova[8] in moderate yield, from the same starting compound by means of triethyl phosphite. They found that the best results (25% yield) were obtained at elevated temperatures.

Aminophosphine 9 did not show high diastereoselectivity in the formation of alkenes, as both *E* and *Z* isomers were found where possible (2, 7, and 8). As is apparent from the results summarized in Table I, the order of reactivity of different halogens is I > Br > Cl > F, also in a highly selective manner. The abstraction of fluorine and bromine was found only in the case of the partially fluorinated alkene 3, and the possible competing reaction of dehydrofluorination was not observed. Finally, 9 differs markedly not only from other reducing agents known to effect dehalogenation, such as phosphites, but even from the very similar tris(dimethylamino)phosphine. The latter did not yield perfluoroallyl chloride under the same conditions or under longer reaction times and higher temperature, although it did give a 1,2 debromination reaction (cf. Table I).

In conclusion, aminophosphines are promising reagents for the synthesis of haloalkenes by selective dehalogenation. The limited examples demonstrated in this work using tris(diethylamino)phosphine suggests many other potential applications for this readily available reagent.

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Supplementary Material Available: ^1H and ^{19}F NMR spectra of 3 and ^{19}F NMR spectra of 6–8 (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

An Improved Procedure for Retro-Cycloaddition of Adducts from Steroidal 5,7-Dienes and 4-Phenyl-1,2,4-triazoline-3,5-dione

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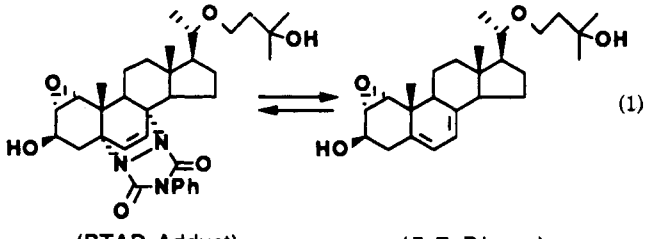
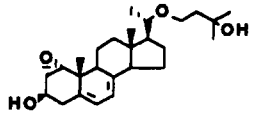
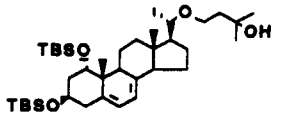
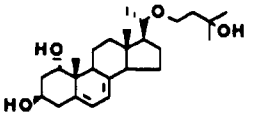
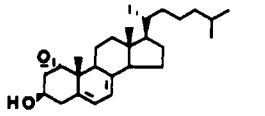
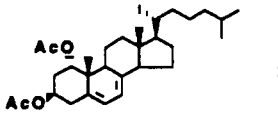
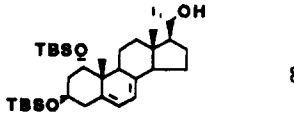
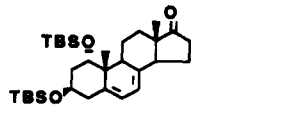
Retro-cycloaddition of adducts from steroidal 5,7-dienes and 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) to regenerate the 5,7-diene systems is one of the most important reactions in the steroid–vitamin D chemistry (eq 1).[1] The



(1)

Table I. Steroidal 5,7-Dienes Prepared from PTAD Adducts by Retro-Cycloaddition (140 °C, DMI)

entry/ compd	reaction time (h)	5,7-dienes	yield[a] (%)	lit.
1	2		84	
2	2		76	5
3	1.5		68	5
4	2.5		87	6
5	1		84	7
6	2.5		87	8
7	5		83	8

[a] Yields refer to pure 5,7-dienes isolated.

formation of the adducts generally proceeds smoothly and quantitatively;[1] however, the yields of the retro-cycloaddition of the adducts are not always satisfactory under the known conditions (e.g., $LiAlH_4$,[1] Na/EtOH,[1] hydrazine hydrate,[1] furan,[1] pyrolysis,[1] K_2CO_3/DMSO or DMF,[2] tetramethylguanidine[3] or γ-collidine,[3] or KOH/EtOH[4]). We now wish to report an improved procedure which involves heating adducts alone in 1,3-dimethyl-2-imidazolidinone (DMI).

In a typical procedure, the PTAD adduct in DMI is stirred at 140 °C for 1–5 h. After the usual workup, the 5,7-diene is obtained in 68–87% yields. The results are summarized in Table I.

When DMF or DMSO was used as a solvent instead of DMI, the retro-cycloaddition of the adducts proceeded very slowly and in poor yields, while in the case of xylene the reaction did not occur. The present procedure for retro-cycloaddition is very useful due to its simplicity and high yield with acid-, base-, or $LiAlH_4$-sensitive substituents remaining intact.

Experimental Section

General Procedure for Retro-Cycloaddition. A solution of the PTAD adduct (entry 1) (327 mg, 0.55 mmol) in DMI (32.7 mL) was stirred at 140 °C (bath temperature) for 2 h. The reaction

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