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Reductive dehalogenation of polyhalofluorocarbons with tributyltin hydride

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Abstract

The reduction of polyhalofluorocarbons, including $ClCF_2CFClCF_2Cl$, $(ClCF_2CFCl)_2$, $ICH_2(CF_2)_3CH_2I$ and vicinal dichloroperfluorocycloalkanes, with tributyltin hydride gave the corresponding hydrofluorocarbons in good to excellent yield. The results are compared with similar reductions with other reducing agents, and to tin hydride reductions of non-fluorinated analogs.

Keywords: Reductive dehalogenation; Polyhalofluorcarbons; Tributyltin hydride; NMR spectroscopy; Hydrofluorocarbons

1. Introduction

Tributyltin hydride (**1**) has become a popular reagent for reductive dehalogenations, including the reductive dechlorination, debromination and deiodination of fluorinated compounds [1]. In most cases, however, the fluorine content in the molecule was relatively low or the fluorine atoms were remote from the reaction site. Since the presence of fluorine near the reaction site can profoundly effect the outcome of a reaction, it was of interest to examine the reductions of a variety of halogenated, highly fluorinated compounds with **1**, and compare them, where possible, to Zn, $LiAlH_4$ and catalytic reductions.

Of particular interest was the reduction of vicinal halogens in highly fluorinated materials. The product of the reduction of vicinal halogens in non-fluorinated compounds with **1** depends on the structure of the molecule and the type of halogen to be reduced. In the cyclohexane series, for example, reduction with **1** leads to dehalogenation: 1,2-dichlorocyclohexane gave cyclohexene and *vic*-dibromotriacetylglucal gave the olefin, triacetylglucal [2]. In contrast, reduction of the vicinal bromines of a cyclobutane derivative with **1** gave the corresponding hydrodebromination product [3]. With linear *vic*-dihalogenated compounds, dehalogenation to an olefin is the major reaction with *vic*-dibromides, but olefin formation is only a minor side reaction for *vic*-dichlorides, which give simple reduction products upon reaction with **1** [4].

Hydrofluorocarbons (HCFs), the products of the reductions in this study, are of current interest for a variety of applications, including anesthetics [5], solvents [6], refrigerants [7] and blowing agents [7].

2. Results and discussion

The reduction of mono-iodofluoroalkanes (**1a–4a**, Table 1) was readily accomplished in good yield using neat **1**; the reduction of **1a** in 86% yield representing a substantial improvement in yield compared to Zn reduction (52% yield) [5]. Although the reduction of compounds of the type R_fCH_2I (R_f = perfluoroalkyl; **2a–4a**) provide the corresponding HFCs in good yield, **1** may not be the reagent of choice, since $LiAlH_4$ reduction of the corresponding tosylates (from which the iodides were derived) also provided the HFCs in good yield [7]. Zinc reduction of $ICH_2CF_2CF_2CF_2CH_2I$ (**5a**) gave a complex mixture containing the cyclic compound 1,1,2,2,3,3-hexafluorocyclopentane as a major product, while $LiAlH_4$ reduction of the di-iodide also gave a complex mixture which contained a diene (GC–MS) as a major product. In contrast, tributyltin hydride reduction provided $CH_3CF_2CF_2CF_2CH_3$ (**5b**) in 79% yield.

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[1] For representative examples of the dehalogenation of fluorine-containing compounds see Ref. [1a–d] and for general reviews see Ref. [1e,f].

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Table 1
Reductions with tributyltin hydride

Reactant	Product	Yield (%) [a]
$CF_3(CF)_5I$ (**1a**)	$CF_3(CF_2)_5H$ (**1b**)	86
$H(CF_2)_4CH_2I$ (**2a**)	$H(CF_2)_4CH_3$ (**2b**)	83
$CF_3CF_2CH_2I$ (**3a**)	$CF_3CF_2CH_3$ (**3b**)	91
$HCF_2CF_2CH_2I$ (**4a**)	$HCF_2CF_2CH_3$ (**4b**)	67
$ICH_2(CF_2)_3CH_2I$ (**5a**)	$CH_3(CF_2)_3CH_3$ (**5b**)	79
cis,trans-dichlorocyclobutane (**6a**)	*cis,trans*-dihydrocyclobutane (**6b**)	71
cis,trans-dichlorocyclopentane (**7a**)	*cis,trans*-dihydrocyclopentane (**7b**)	67
$ClCF_2CFClCF_2Cl$ (**8a**)	HCF_2CFHCF_2H (**8b**)	80
$ClCF_2CFClCFClCF_2Cl$ (**9a**)	$HCF_2CFHCFHCF_2H$ (**9b**)	98
$ClCF_2CFClCFClCF_2Cl$ (**9a**)	$ClCF_2CFHCFClCF_2Cl$ (**10**)	36
$ClCF_2CFClCF_2CFCl_2$ (**11a**)	$HCF_2CFHCF_2CH_2F$ (**11b**)	69
$Cl_2CFCF_2CF_2CFCl_2$ (**12a**)	$FCH_2CF_2CF_2CH_2F$ (**12b**)	90 [b]

[a] Isolated yields.
[b] GC yield.

trans-1,2-Dihydroperfluorocycloalkanes, which have boiling points substantially lower than their *cis* isomers, are perhaps best prepared by the tin hydride reduction of the corresponding dichlorides, as catalytic reduction of the olefin leads primarily to the *cis* isomer. Obtaining pure products via the reduction of 1,2-dichlorohexafluorocyclobutane (**6a**) with $LiAlH_4$ in THF or dibutyl ether was reportedly difficult, although *trans*-**6b** was obtained in about 37% yield using $LiAlH_4$ in ether [8]. Tributyltin hydride reduction of a *cis*/*trans* mixture of **6a** gave primarily *trans*-**6b** (41% distilled yield).

Reduction of 1,2-dichloroperfluorocyclopentane (**7a**) with $LiAlH_4$ gave the corresponding HFCs in a 4.6:1 ratio (mainly the *cis* isomer) in 64% yield [9]. Reduction with **1** resulted in a similar yield of **7b**, although no solvent was required and the product (mainly *trans*) was obtained by direct distillation from the reaction mixture. This result contrasts sharply with the dechlorination of 1,2-dichlorocyclohexane to cyclohexene using **1** in hot xylene [2].

In the reduction of linear chlorofluorocarbons (CFCs) with two or more vicinal chlorines, reduction with zinc can lead to olefins and catalytic reductions can be complex, resulting from rearrangements and/or reductive defluorinations. While the reduction of $ClCF_2CFClCF_2Cl$ (**8a**) reportedly failed with $LiAlH_4$ [7], tributyltin hydride cleanly reduced both $ClCF_2CFClCF_2Cl$ and $ClCF_2CFClCFClCF_2Cl$ to the corresponding HFCs in good yield. Slow addition of 1 equiv. of tributyltin hydride to $ClCF_2CFClCFClCF_2Cl$ (**9a**) at 0–5 °C gave the trichloride **10** in 78% selectivity, indicating a preference for reduction of the secondary chlorine.

The two diastereomers arising from complete reduction of the tetrachloride **9a** were separable by careful distillation and were obtained in 27% (98.9% purity) and 25% (99.8% purity) distilled yields, respectively. This can be compared to the yields of the same from the catalytic reduction of perfluorobutadiene [5], which gave the diastereomers in 11% and 19% distilled yields, presumably reflecting a cleaner crude reaction mixture in the tin hydride reduction.

As indicated above in the reduction of **8a**, $LiAlH_4$ reduction of linear CFCs and HCFCs is not always reliable and separation of ether solvents can be difficult [3,8,10]. Further support for this conclusion is the fact that in the $LiAlH_4$ reduction of $CF_3CFClCFClCF_3$, the normal reduction products were obtained in 55% yield while the reduction of $HCF_2CF_2CFClCF_2Cl$ provided $HCF_2CF_2CHFCF_2H$ in rather low (<10%) yield [10]. Olefin formation and subsequent reaction with $LiAlH_4$ was suggested as a cause for the low yield.

Commercial samples of **11a** were only about 74% pure by GC analysis. Major impurities were identified as $Cl_2CFCF_2CF_2CFCl_2$ (20%) and $ClCF_2CFClCFClCF_2Cl$ (4%). Reduction with **1** thus gave, in addition to HFC **11b**, $FCH_2CF_2CF_2CH_2F$ (**12b**) and **9b**.

In the reduction of **9a**, **11a** and **12a**, no radical initiators were required. This contrasts the normal reduction of alkyl chlorides with **1** for which UV irradiation or radical initiators (e.g. AIBN, 80 °C) are typically employed. When the CFCs were added to neat **1** at room temperature, an exotherm occurred and reaction temperatures of about 100 °C could be maintained by controlling the rate of addition.

Although the reduction of linear CFCs having vicinal chlorines parallels the reduction of their non-fluorinated analogs (i.e. hydrodechlorination), a significant difference was observed for vicinal dibromides. In contrast to the reduction of alkyl *vic*-dibromides with **1** (which gave olefins in high yield under a variety of conditions [4]), the reduction of $CF_3CFBrCF_2Br$ resulted primarily (ca. 75%) in hydrodebromination products (CF_3CHFCF_2H, CF_3CHFCF_2Br and $CF_3CFBrCF_2H$), although some debromination product ($CF_3CF{=}CF_2$) was also observed. This difference is consistent with the recent findings of Avila et al. [11], who determined that perfluoroalkyl radicals abstract hydrogen from **1** about 100-times faster than n-alkyl radicals. Another factor which favors dehydrobromination in the reduction of $CF_3CFBrCF_2Br$ is the destabilization of C=C double bonds by fluorine, which has been estimated [12] at about 5 kcal mol^{-1} per fluorine. In the present case, formation of perfluoropropene is thus estimated to be 15 kcal mol^{-1} less favorable than the formation of propene from its dibromide.

3. Experimental details

^1H NMR spectra were determined for $CDCl_3$ solutions and ^{19}F NMR spectra in the same solvent with internal $CFCl_3$, using either a Varian EM-390 or Varian Unity 300 MHz spectrometer. ^{19}F NMR data are reported as ppm upfield (negative values) from $CFCl_3$.

Tributyltin hydride was obtained from Aldrich Chemical Co. and used as received. The commercially available alcohols used to make **2b**–**5b** were converted to the corresponding iodides [13,14] via the tosylates [7,13,15].

The preparation of **5b** is representative of a typical procedure for the tributyltin hydride reduction of the iodides.

3.1. 1,5-Di-iodo-2,2,3,3,4,4-hexafluoropentane (5a)

The ditosylate of 2,2,3,3,4,4-hexafluoropentan-1,5-diol [15] (110.6 g, 0.213 mol), 103.1 g (0.688 mol) of NaI and 300 ml of diethylene glycol were heated with mechanical stirring at 160 °C for 20 h. After cooling, 200 ml of water was added and the mixture extracted twice with 350 ml of ether. The combined ether extracts were washed with dilute aq. $NaHSO_3$, stirred over activated carbon and dried ($MgSO_4$). Removal of the solvent under reduced pressure gave 90.2 g of the crude di-iodide. Recrystallization from petroleum ether gave 61.3 g (67% yield) of pure 1,5-di-iodo-2,2,3,3,4,4-hexafluoropentane. ^1H NMR δ: 3.8 (t, $J=12$ Hz) ppm. ^{19}F NMR δ: -107.5 (4F); -124 (2F) ppm. This is essentially the method of Ref. [14].

3.2. 2,2,3,3,4,4-Hexafluoropentane (5b)

A 100 ml flask fitted with a heated addition funnel and a distillation column with take-off head was charged with 35 ml (37.9 g, 0.13 mol) of tributyltin hydride (N_2 atmosphere). The di-iodide ($ICH_2CF_2CF_2CF_2CH_2I$, 24.7 g, 0.057 mol) was added from the addition funnel (as a melt) at a rate to keep the temperature below 40 °C. After addition was complete, the mixture was refluxed for 2 h and the product distilled directly. The last of the product was removed under reduced pressure. Redistillation (micro spinning band column) provided 8.13 g (79% yield) of 99.8% pure 2,2,3,3,4,4-hexafluoropentane (**5b**), b.p. 61.5 °C. ^1H NMR δ: 1.8 (t) ppm. ^{19}F NMR δ: -106.5 (4F); -128.5 (2F) ppm. MS *m/z* (%): 165 (2.9); 161 (0.4); 145 (0.9); 115 (1.7); 96 (53.2); 95 (41.3); 65 (100); 45 (26.3).

3.3. trans-1,2-Dihydrohexafluorocyclobutane

To 127 ml (0.472 mol) of tributyltin hydride (N_2 atmosphere) was added 50.2 g (0.216 mol) of 1,2-dichloroperfluorocyclobutane over a period of 3 h while maintaining the temperature at 25–30 °C. Distillation at atmospheric pressure gave 17.9 g of primarily (93%) *trans* isomer and distillation of the residue under reduced pressure gave an additional 7.3 g of product, for a total of 25.2 g (71% yield). Redistillation gave the pure *trans* isomer, b.p. 27 °C (lit. value [16]: b.p. 27 °C) in 41% yield. ^1H NMR δ: 5.2 (dm, $J_{H-C-F}=50$ Hz) ppm. ^{19}F NMR δ: -123.7 (2F, $J_{F-C-F}=240$ Hz); -135.8 (2F, $J_{F-C-F}=240$ Hz); -211.0 (2F, $J_{H-C-F}=50$ Hz) ppm.

3.4. cis- and trans-1,2-Dihydro-octafluorocyclopentane (7b)

1,2-Dichloroperfluorocyclopentane (39.2 g, 0.139 mol) was added to 47 ml (0.173 mol) of tributyltin hydride at 100 °C, during which time 20 g of a 2:7 mixture of *cis* and *trans*-1,2-dihydroperfluorocyclopentane (67% yield based on dichloride) distilled out. Redistillation gave the *trans* isomer, b.p. 47 °C (lit. value [9]: b.p. 50 °C) [^1H NMR δ: 4.9 (dm, $J_{H-C-F}=48$ Hz) ppm] and the *cis* isomer, b.p. 77–78 °C (lit. value [9]: b.p. 78 °C) contaminated with about 15% of the *trans* isomer.

3.5. 1,1,2,3,3-Pentafluoropropane (8b)

A 750 ml Teflon-lined autoclave was charged with 5.0 g of AIBN, sealed and evacuated. Tributyltin hydride (433 g, 1.49 mol) was charged under N_2 pressure. The autoclave was cooled to 0 °C, evacuated and charged with 98.5 g (0.416 mol) of 1,2,3-trichloropentafluoropropane. Upon warming to 31 °C, an exotherm occurred (to 177 °C, 190 psig) which subsided rapidly. The contents were stirred overnight at 110 °C. After cooling, the product was distilled directly from the crude mixture to give 49.5 g (90% purity; 80% yield). Redistillation provided 97% pure material, b.p. 37–40 °C (lit. value [17]: b.p. 44 °C). ^1H NMR δ: 4.1–5.1 (dm, 1H); 6.02 (2H) ppm. ^{19}F NMR δ: -134 (4F); -223 (1F) ppm.

3.6. 1,2,3,4-Tetrachloroperfluorobutane (9a)

This procedure is a modification of the procedure of Henne and Postelneck [18] who obtained $ClCF_2CFClCFClCF_2Cl$ in 51% yield.

A 2-l, three-necked flask, fitted with a mechanical stirrer and Dry Ice condenser, was charged with 550.4 g (1.97 mol) of $ClCF_2CClFI$, 240 ml of CH_2Cl_2 and 240 ml of acetic anhydride. The mixture was brought to 45 °C and 10 g of powdered Zn added. After the resulting exotherm (to about 60 °C) had subsided, an additional 10 g of Zn was added. This was repeated until a total of 130.8 g (2 mol) of Zn had been added over a period of 2 h. Heating and stirring were continued for 0.25 h before cooling and filtering the mixture. The filtrate was hydrolyzed by the slow addition (ice bath cooling) of 600 ml of 2 N H_2SO_4. The organic layer was separated, neutralized with 1200 ml of 10% NaOH, washed with 600 ml of aq. NaCl and dried ($MgSO_4$). After removing the bulk of the CH_2Cl_2 by atmospheric distillation, the residue was distilled at 70 mmHg pressure to give 210.4 g of $ClCF_2CFClCFClCF_2Cl$ (0.692 mol, 70.1% yield, GC purity 99.4%), b.p. 59–61 °C (lit. value [18]: 133–135 °C). ^{19}F NMR δ: -61.7 (2F); -121.9 (1F) ppm.

3.7. *1,1,2,3,4,4-Hexafluorobutane (9b)*

A 2-l, three-necked flask, fitted with an efficient 0 °C condenser, was charged with 1071 g (3.68 mol) of tributyltin hydride. 1,2,3,4-Tetrachlorohexafluorobutane (243 g, 0.80 mol) was added over 45 min, during which time the temperature rose to 130 °C. The mixture was refluxed for an additional 2 h. The product was removed from the $^n Bu_3SnCl$ residue by vacuum transfer to a -78 °C receiving flask to give 131 g (98% yield) of 97% pure $HCF_2CHFCHFCF_2H$. Distillation provided a 99% pure mixture of the D,L and *meso* isomers, b.p. 61–68 °C (lit. value [5]: 61–63.2 °C and 67–68.2 °C). Spectral data were consistent with those previously reported [5]. Separation into the component isomers using a 3 ft. packed ('Heli-pak', 0.05×0.1×0.1 in. Nichrome mesh) column gave 35.3 g (26.6% yield, 98.9% pure) b.p. 61–62 °C and 32.8 g (24.7% yield, 99.8% pure) b.p. 68 °C.

3.8. *1,2,4-Trichloro-1,1,2,3,4,4-hexafluorobutane (10)*

Tributyltin hydride was added in about 10 equal increments over a 6 h period (0.152 mol total) to 46.1 g (0.152 mol) of 98% pure **9a** at 0–5 °C. The crude product was removed from tributyltin chloride by vacuum transfer (31.5 g). Analysis by GC indicated this consisted of 62% of a trichloride, 15% starting material and 4% tributyltin chloride (78% selectivity for the trichloride). Distillation provided 14.9 g of 96.3% pure 1,2,4-trichloro-1,1,2,3,4,4-hexafluorobutane, b.p. 106 °C. Due to the presence of two chiral centers, the observed ^{1}H NMR spectrum was a composite of *R,S*/*S,R* and *R,R*/*S,S* spectra. One was assigned to δ 5.17 (dddd, J=43.5, 15.6, 10.5, 3.0 Hz) ppm; the other to δ 5.21 (dddd, J=43.8, 10.2, 5.4, 1.5 Hz) ppm. ^{19}F NMR δ: one isomer: -60.9 (1F of $-CF_2Cl$, $J_{F-C-F}=175.8$ Hz); -63.9 (1F of $-CF_2Cl$); -189.5 ($-\mathrm{C}F\mathrm{H}$); -129.8 ($-\mathrm{C}F\mathrm{Cl}$); -66.9 (2F, $-CF_2Cl$) ppm; other isomer: -57.2 (1F of $-CF_2Cl$, $J_{F-C-F}=176.3$ Hz); -63.0 (1F of $-CF_2Cl$); -189.0 ($-\mathrm{C}F\mathrm{H}$); -137.4 ($-\mathrm{C}F\mathrm{Cl}$); -65.9 (2F, $-CF_2Cl$) ppm.

3.9. *1,1,2,3,3,4- (11b) and 1,2,2,3,3,4-Hexafluorobutane (12b)*

Reduction of a commercial sample of **11a** (containing ca. 4% of **9a**, 74% of **11a** and 20% of **12a**) with **1** was conducted in a manner similar to that described for **9b**. GC yields were 94% for **11b** and 90% for **12b**. After removing the products from the tributyltin chloride by-product, distillation through a 5 ft. packed column gave 1,1,2,3,3,4-hexafluorobutane (**11b**) in 69% yield and 96% purity (b.p. 68 °C, impurities were 3% of **12b** and 1% of **9b**) and 82% pure 1,2,2,3,3,4-hexafluorobutane (**12b**), b.p. 70–71 °C (containing 18% of **11b**). The ^{1}H and ^{19}F NMR spectra of **11b** and **12b** were consistent with those reported [10], except that in $CDCl_3$ solution the magnetic non-equivalence of the two diastereotopic $\mathrm{H}\mathrm{C}F_2\mathrm{CFH}-$ fluorines in **11b** were manifested by a 312 Hz geminal coupling constant not reported earlier. ^{13}C NMR δ: **11b**: 110.4 ($-\mathit{C}\mathrm{F_2H}$, $J_{CF}=245$ Hz); 85.2 ($-\mathit{C}\mathrm{FH}-$, $J_{CF}=190$ Hz); 116.1 ($-\mathit{C}\mathrm{F_2}-$, $J_{CF}=250$ Hz); 78.6 ($-\mathit{C}\mathrm{H_2F}$, $J_{CF}=177$ Hz) ppm.

3.10. *Reduction of 1,2-dibromohexafluoropropane*

1,2-Dibromohexafluoropropane (31.7 g, 0.10 mol) was placed in a flask (N_2 atmosphere) fitted with a distillation column and take-off head which was connected to a -78 °C cold trap. The flask was placed in an oil bath, but no external heat was applied as 32.7 g (0.11 mol) of tributyltin hydride was added over 1.5 h. The mixture was then refluxed for 1.5 h while distilling off the product. The distillate (6.6 g) contained 3% of $CF_3CF{=}CF_2$, 14% of CF_3CHFCF_2H, 21% of $CF_3CFBrCF_2H$ [^{1}H NMR δ: 6.0 (dt, J=4, 54 Hz) ppm], 53% of CF_3CHFCF_2Br [^{1}H NMR δ: 5.0 (dm, J=45 Hz) ppm] and 6% of $CF_3CFBrCF_2Br$. The cold trap (7.3 g) contained 31% of $CF_3CF{=}CF_2$, 44% of CF_3CHFCF_2H and 20% of C_3HBrF_6 isomers. Hydrodebromination products thus account for approximately 75% of the tin hydride added.

4. Conclusions

The reaction of polyhalogenated fluorocarbons with tributyltin hydride proved to be a reliable method for the preparation of HFCs, including those involving the reductive dechlorination of vicinal dichlorides of both linear and cyclic compounds. The use of neat 1 for the reduction of CFCs and HCFCs, while relatively expensive [2] is characterized by simple procedures and product isolation, good to excellent yields and high selectivity for hydrodehalogenation.

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References

[1] (a) N.O. Brace, *J. Fluorine Chem., 20* (1982) 313; (b) M. Van Der Puy, *J. Fluorine Chem., 61* (1993) 133; (c) L.J. Altman and J.C. Vederas, *Chem. Commun.,* (1969) 895; (d) H. Suga, T. Hamatani, Y. Guggisberg and M. Schlosser, *Tetrahedron, 46* (1990) 4255; (e) H.G. Kuivila, *Synthesis,* (1970) 499; (f) W.P. Neumann, *Synthesis,* (1987) 665.

[2] T.-S. Lin, J.-H. Yang, M.-C. Liu and J.-L. Zhu, *Tetrahedron Lett., 31* (1990) 3829.

[3] A. Sanders and W.P. Giering, *J. Org. Chem., 38* (1973) 3055.

[4] R.J. Strunk, P.M. DiGiacomo, K. Aso and H.G. Kuivila, *J. Am. Chem. Soc., 92* (1970) 2849.

[5] T. Hudlicky, R. Fan, J. Reed, D. Carver, M. Hudlicky and E.I. Eger II, *J. Fluorine Chem., 59* (1992) 9.

[6] M. Van Der Puy, A.J. Poss, P.J. Persichini and L.A.S. Ellis, *J. Fluorine Chem., 67* (1994) 215.

[7] D.D. DesMarteau, A.L. Beyerlein, S.-H. Hwang, Y.-C. Shen, S.-W. Li, R. Medonca, K.N. Naik, N.D. Smith and P. Joyner, *Abs. Int. Conf. CFC and Halon Alternatives,* Baltimore, MD, Dec. 3–5, 1991.

[8] M.W. Buxton and J.C. Tatlow, *J. Chem. Soc.,* (1954) 1177.

[9] R.J. Heitzman, C.R. Patrick, R. Stevens and J.C. Tatlow, *J. Chem. Soc.,* (1963) 281.

[10] J. Burdon, S.T. Ezmirly and T.N. Huckerby, *J. Fluorine Chem. 40* (1988) 283.

[11] D.V. Avila, K.U. Ingold, J. Lusztyk, W.R. Dolbier, Jr., H.-Q. Pan and M. Muir, *J. Am. Chem. Soc., 116* (1994) 99.

[12] H.E. O'Neal and S.W. Benson, *J. Phys. Chem., 72* (1968) 1866.

[13] G.V.D. Tiers, H.A. Brown and T.S. Reid, *J. Am. Chem. Soc., 75* (1953) 5978.

[14] G.I. Matyushecheva, N.I. Galkina, N.M. Rastorgueva and L.M. Yagupol'skii, *J. Org. Chem. USSR (Engl. Trans.), 7* (1971) 1704.

[15] S.E. Wentworth and P.L. Sciaraffa, *Org. Prep. Proced., 1* (1969) 225.

[16] W.M. Hutchinson, US Pat. 3 850 759, 1974.

[17] J. Burdon, G.E. Chivers, E.F. Mooney and J.C. Tatlow, *J. Chem. Soc., C,* (1969) 1739.

[18] A.L. Henne and W. Postelneck, *J. Am. Chem. Soc., 77* (1955) 2334.

[19] E.J. Corey and J.W. Suggs, *J. Org. Chem., 40* (1975) 2554.

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[2] Some catalytic processes have proven successful, see Refs. [3,19].