Journal of Fluorine Chemistry, 5 (1975) 135 - 139

SYNTHESIS OF PERFLUORO-t-BUTYL ESTERS FROM ACID FLUORIDES AND POTASSIUM PERFLUORO-t-BUTOXIDE

NYAL S. WALKER and DARRYL D. DESMARTEAU

Department of Chemistry, Kansas State University, Manhattan, Kansas 66506 (U.S.A.)

(Received April 15, 1974)

Summary

Reactions of potassium perfluoro-t-butoxide with acyl fluorides lead to the corresponding perfluoro-t-butyl esters in high yield. The compounds $[(CF_3)_3CO]_2CO$, $(CF_3)_3COC(O)F$, $CF_3C(O)OC(CF_3)_3$, $CH_3C(O)OC(CF_3)_3$ and $CF_3OOC(O)OC(CF_3)_3$ have been thus obtained and some physical and chemical properties of each are reported.

Introduction

Aliphatic perfluorinated esters have only recently been synthesized in any variety by reactions of perfluoroacyl fluorides with metal fluorides and perfluoroalkoxides. A series of heptafluoroisopropoxide esters was obtained and these compounds were found to be quite stable when pure but were catalytically decomposed by fluoride ions at 22 °C [1]. During the study of reactions of potassium perfluoro-t-butoxide with strong oxidizing agents [2], we observed the formation of perfluoro-t-butyl esters when these reactions gave rise to carbonyl fluoride and other acyl fluorides. It appeared that the esters were formed by reaction of the acyl fluoride with excess $KOC(CF_3)_3$ present in the reaction mixture. Subsequent work confirmed that this was the case and an exploitation of this reaction for the synthesis of new $(CF_3)_3CO$-containing esters was initiated.

In this paper, the simple, one-step, high-yield syntheses of a variety of $(CF_3)_3CO$-containing esters of the type $RC(O)OC(CF_3)_3$($R = CF_3OO$, CF_3, CH_3, F, $(CF_3)_3CO$) are reported and properties of the new compounds are given. During the course of this work, three papers have appeared describing related, but different methods for the synthesis of aliphatic fluorinated esters [3 - 5]. Two of the compounds obtained by us, *i.e.* $[(CF_3)_3CO]_2CO$ [4] and $CF_3C(O)OC(CF_3)_3$ [5], were also prepared in these investigations. We have also learned of an earlier unpublished synthesis of $[(CF_3)_3CO]_2CO$ [6].

Experimental

General

A description of the experimental set-up for carrying out this work has been given in the preceeding paper [2].

Reagents

$KOC(CF_3)_3$ was synthesized as described previously [2]. The acyl fluorides $CF_3C(O)F$ and $CH_3C(O)F$ were obtained from PCR, Inc. Carbonyl fluoride and CF,OOC(O)F were synthesized by literature methods [7].

Reactions

The reactions of $KOC(CF_3)_3$ with acid fluorides are summarized in Table 1. These were carried out by condensing the acyl fluoride on to the $KOC(CF_3)_3$ at -196 °C, followed by warming to the appropriate reaction temperature. Products were then separated by trap-to-trap distillation. Additional data on the compounds are as follows:

$[(CF_3)_3CO]CO$: b.p., 119.7 °C; m.p., 43.0 °C; mol wt., 501.7, calcd., 498.06; IR: 3715 (vw), 2570 (vw), 2465 (vw), 2395 (vw), 2375 (vw), 2200 (vw), 2110 (vw), 1873 (sh), 1863 (s), 1818 (w), 1798 (vw), 1710 (vw), 1637 (vw), 1598 (vw), 1556 (vw), 1507 (vw), 1418 (vw), 1280 (vs), 1229 (w), 1215 (vw), 1189 (w), 1175 (s), 1140 (w), 1095 (s), 1010 (s), 987 (s), 938 (w), 796 (w), 780 (vw), 770 (m), 750 (m), 730 (s), 720 (s), 700 (m), 618 (w), 570 (w), 538 (m), 475 (m) cm-i; NMR: ϕ^* 70.20 ppm [s, $(CF_3)_3CO$]; $\Delta H_{vap} = 9.49$ kcal mol^{-1}; AS,,, = 24.2 cal K^{-1}mol^{-1}; log P (mmHg) = 8.1625 — 2074.8/T (43 - 85 “C); v.p. (solid) = 20.6 mmHg (31.4 “C).

$(CF_3)_3COC(O)F$: b.p., 46.1 °C; mol.wt., 279.8, calcd., 282.01; IR: 3768 (vw), 3110 (vw), 3045 (vw), 2918 (vw), 2841 (vw), 2575 (vw), 2470 (vw), 2394 (vw), 2365 (vw), 2335 (vw), 2244 (vw), 2218 (vw), 2170 (vw), 2142 (vw), 2090 (vw), 2050 (vw), 1955 (w), 1915 (sh), 1900 (s), 1878 (sh), 1849 (w), 1770 (vw), 1735 (vw), 1684 (vw), 1604 (vw), 1554 (vw), 1518 (w), 1450 (w), 1278 (vs), 1227 (w), 1207 (s), 1182 (w), 1149 (m), 1095 (vw), 1069 (vw), 1011 (s), 984 (s), 938 (m), 800 (vw), 743 (m), 728 (m), 703 (w), 658 (m), 569 (vw), 534 (m) cm^{-1}; NMR: ϕ^* 70.31 ppm [d, $(CF_3)_3CO$], 73.80 ppm [dectet, $C(O)F$], J(FF) = 1.2 Hz; AH,,, = 7.70 kcal mol^{-1}; ΔS_{vap} = 24.1 cal K^{-1}mol^{-1}; log P (mmHg) = 8.1531 — 1683.2/T (2 - 32 “C).

$(CF_3)_3COC(O)CF_3$: b.p., 54.9 °C, mol.wt., 329.2, calcd., 332.04; IR: 2690 (vw), 2590 (vw), 2460 (vw), 2395 (w), 2317 (vw), 2250 (vw), 2194 (vw), 2143 (vw), 2084 (vw), 2056 (vw), 2040 (vw), 2000 (vw), 1964 (vw), 1930 (vw), 1896 (w), 1854 (s), 1807 (vw), 1741 (vw), 1698 (vw), 1580 (vw), 1559 (vw), 1514 (w), 1488 (vw), 1460 (vw), 1423 (vw), 1333 (s), 1285 (vs), 1248 (m), 1200 (s), 1128 (s), 1073 (m), 1006 (s), 989 (s), 839 (m), 770 (w), 753 (m), 730 (m), 714 (m), 668 (m), 574 (w), 540 (m), 503 (m), 421 (w) cm^{-1}

TABLE 1

Reactions of $KOC(CF_3)_3$ with acyl fluorides

$KOC(CF_3)_3$[a]	Reactant[a]	Conditions	Product	(Yield)[b]
3.4	COF_2, 17.7	22 °C, 24 h	$(CF_3)_3COC(O)F$, $[(CF_3)_3CO]_2CO$	(50) (22)[c]
3.2	$CF_3C(O)F$, 3.3	22 °C, 20 h	$CF_3C(O)OC(CF_3)_3$	(78)[d]
3.1	$CH_3C(O)F$, 3.2	38 °C, 24 h	$CH_3C(O)F$	(79)[e]
1.5	$CF_3OOC(O)F$, 1.0	22 °C, 2 h	$CF_3OOC(O)OC(CF_3)_3$	(50)[f]

[a] Amounts in mmoles.
[b] Yields (%) based on the amount of $KOC(CF_3)_3$.
[c] Collected at −90 °C and −40 °C respectively.
[d] Collected at −111 °C.
[e] Collected at −78 °C.
[f] Collected at −65 °C after passing through a −40 °C trap.

NMR: ϕ^* 70.14 ppm [s, $(CF_3)_3CO$], 75.29 ppm [s, CF_3]; ΔH_{vap} = 8.21 kcal mol^{-1}; ΔS_{vap} = 25.0 cal K^{-1} mol^{-1}; $\log P$ (mmHg) = 8.3480 − 1793.8/T (−9 °C to 25 °C).

$(CF_3)_3COC(O)CH_3$: b.p., 85.0 °C; mol.wt., 277.6, calcd., 278.07; IR: 3642 (w), 3039 (vw), 3004 (vw), 2960 (vw), 2852 (vw), 2700 (vw), 2550 (vw), 2480 (vw), 2420 (vw), 2390 (vw), 2360 (vw), 2335 (vw), 2308 (vw), 2290 (vw), 2240 (vw), 2165 (vw), 2145 (vw), 2035 (vw), 1984 (vw), 1928 (vw), 1888 (vw), 1831 (s), 1790 (w), 1722 (vw), 1585 (vw), 1495 (vw), 1436 (w), 1375 (m), 1275 (vs), 1174 (s), 1122 (s), 1014 (s), 986 (s), 860 (m), 769 (m), 735 (s), 686 (w), 594 (m), 540 (m), 504 (m), 461 (vw) cm^{-1}; NMR: ϕ^* 70.08 ppm [s, $(CF_3)_3CO$], δ 2.37 ppm [s, CH_3]; ΔH_{vap} = 9.57 kcal mol^{-1}; ΔS_{vap} = 26.7 cal K^{-1} mol^{-1}; $\log P$ (mmHg) = 8.7218 − 2092.3/T (0 - 55 °C).

$(CF_3)_3COC(O)OOCF_3$: b.p., 79.8 °C; mol.wt., 361.5, calcd., 364.04; IR: 3745 (vw), 2584 (vw), 2530 (vw), 2475 (vw), 2430 (vw), 2400 (vw), 2375 (vw), 2351 (vw), 2220 (vw), 2170 (vw), 2150 (vw), 2123 (vw), 2060 (vw), 1900 (sh), 1884 (s), 1865 (s), 1736 (vw), 1681 (vw), 1558 (vw), 1500 (vw), 1416 (vw), 1290 (vs), 1242 (s), 1189 (m), 1150 (s), 1116 (m), 1072 (w), 1017 (s), 984 (s), 924 (m), 903 (vw), 888 (vw), 746 (m), 731 (m), 700 (vw), 664 (w), 611 (w), 590 (w), 570 (vw), 538 (m), 459 (m), 435 (vw) cm^{-1}; NMR: ϕ^* 70.32 ppm [s, $(CF_3)_3CO$], 69.60 ppm [s, CF_3OO]; ΔH_{vap} = 8.00 kcal mol^{-1}; ΔS_{vap} = 22.6 cal K^{-1} mol^{-1}; $\log P$ (mmHg) = 7.8216 − 1748.3/T (0 - 42 °C).

Results and discussion

The reactions of $KOC(CF_3)_3$ with acyl fluorides provide a convenient new method for the synthesis of perfluoro-t-butyl esters.

$$RC(O)F + KOC(CF_3)_3 \rightarrow RC(O)O(CF_3)_3 + KF$$

$$(R = F, CF_3, CH_3, CF_3OO, (CF_3)_3CO)$$

The reactions proceed readily in high yield without the use of solvents. When the ease with which $KOC(CF_3)_3$ is prepared is taken into account, this method should have wide applicability. The examples demonstrated do not fully define the scope of the reaction but it is probably quite general.

The mechanism for this reaction can be viewed as a nucleophilic displacement of fluoride by the $(CF_3)_3CO^-$ ion. As long as the R group is not readily displaced by nucleophilic reagents the desired product is obtained. With COF_2, displacement of the second fluoride occurs readily and an excess of COF_2 is required in order to obtain appreciable yields of the monosubstituted derivative. Excess acyl fluoride and increased reaction temperatures increase the rate and yields of the reaction except in the case of $CF_3OOC(O)F$. In this case the product is somewhat unstable in the presence of $KOC(CF_3)_3$, forming $[(CF_3)_3CO]_2$ and an unidentified material of high molecular weight (*ca.* 500 - 600) containing —C(O)—, CF_3OO— and $(CF_3)_3CO$— groups.

The perfluoro-t-butyl esters are all stable at 22 °C and readily handled in both glass and metal vacuum systems. The thermal stability of all the compounds is probably high. Both $CH_3C(O)OC(CF_3)_3$ and $CF_3C(O)OC(CF_3)_3$ are stable at 275 °C in glass and heating $CF_3C(O)OC(CF_3)_3$ to 500 °C did not cause appreciable decomposition. This very high thermal stability was unexpected as the formation of hexafluoroacetone as a decomposition product was anticipated at lower temperatures.

The IR spectra of the new compounds contain characteristic carbonyl stretching frequencies ranging from 1900 cm^{-1} for $(CF_3)_3COC(O)F$ to 1831 cm^{-1} for $CH_3C(O)OC(CF_3)_3$. As observed for other $(CF_3)_3CO$ derivatives the spectra show very characteristic bands for this group [2]. The ^{19}F NMR spectra of all these compounds contain chemical shifts ϕ^* at *ca.* 70 ppm characteristic of the $(CF_3)_3CO$ group. The highest value was observed for $(CF_3)_3COC(O)F$ and the lowest for $CH_3C(O)OC(CF_3)_3$. These and other results indicate that the chemical shift of the $(CF_3)_3CO$ group is sensitive to the electron-withdrawing capacity of the attached group. In Table 2 a compilation of ϕ^* values for a variety $(CF_3)_3CO$ derivatives is given. An obvious trend of decreasing chemical shift with increased electron withdrawal is evident. The lowest value is observed for $[(CF_3)_3CO]_3B$ and this is consistent with the ability of B to accept electron density from oxygen into the vacant 2p boron orbital. Conversely, the highest value is found for $(CF_3)_3COH$, followed closely by $(CF_3)_3COCH_2CH_2Cl$, reflecting the poor electron-withdrawing ability of these groups.

Acknowledgements

The support of this research by the Donors of the Petroleum Research Fund, administered by the American Chemical Society and by the National Science Foundation, is gratefully acknowledged.

TABLE 2

^{19}F chemical shifts of $(CF_3)_3CO$ derivatives[a]

$(CF_3)_3COH$, 75.0[b]
$(CF_3)_3COCH_2CH_2Cl$, 74.4[c]
$[(CF_3)_3CO]_2PF_3$, 71.4[d]
$(CF_3)_3COPF_4$, 71.4[d]
$(CF_3)_3COCF_2CF_2Cl$, 70.3[c]
$(CF_3)_3COC(O)OOCF_3$, 70.3[b]
$(CF_3)_3COC(O)F$, 70.3[b]
$[(CF_3)_3CO]_2CO$, 70.2[b]
$(CF_3)_3COC(O)CF_3$, 70.1[b]
$(CF_3)_3COC(O)CH_3$, 70.1[b]
$(CF)_3COCl$, 70.1[e]
$(CF_3)_3COC(O)Cl$, 70.0[e]
$[(CF_3)_3CO]_2$, 70.0[b]
$(CF_3)_3COSO_2Cl$, 69.5[e]
$(CF_3)_3COF$, 69.5[f]
$(CF_3)_3COOSO_2F$, 69.3[b]
$(CF_3)_3CONO_2$, 69.1[b]
$[(CF_3)_3CO]_3B$, 68.1[g]

[a] ϕ^* values to the nearest 0.1 ppm.

[b] This work.

[c] L. R. Anderson, D. E. Young, D. E. Gould, R. Jurrik-Hogan, D. Nuechterlin and W. B. Fox, J. Org. Chem., 35 (1970) 3730.

[d] D. E. Young and W. B. Fox, Inorg. Nucl. Chem. Lett., 7 (1971) 1033.

[e] D. E. Young, L. R. Anderson, D. E. Gould and W. B. Fox, J. Amer. Chem. Soc., 92 (1970) 2313.

[f] J. H. Prager and P. G. Thompson, J. Amer. Chem. Soc., 87 (1965) 230.

[g] D. E. Young, L. R. Anderson and W. B. Fox, Inorg. Chem., 10 (1971) 2810.

References

1 R. A. DeMarco, D. A. Conch and J. M. Shreeve, J. Org. Chem., 37 (1972) 3332.
2 N. S. Walker and D. D. DesMarteau, J. Fluorine Chem., 5 (1975) 000.
3 A. Majid and J. M. Shreeve, J. Org. Chem., 38 (1973) 4028.
4 R. J. DePasquale, J. Org. Chem., 38 (1973) 3025.
5 P. G. Johnson and B. Tittle, J. Fluorine Chem., 3 (1973/74) 1.
6 W. B. Fox, private communication. Many other reactions leading to the formation of $(CF_3)_3CO$ derivatives have been carried out by Fox and co-workers.
7 D. D. DesMarteau, Inorg. Chem., 9 (1970) 2179.