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A New Synthesis of Ketones Containing One Perfluoroalkyl Group[1,2]

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The reactions of perfluorinated acids ($C_nF_{2n+1}CO_2H$, $n = 1$–3) with Grignard reagents give mixtures of ketones and carbinols containing one perfluoroalkyl group with the ketones being the major products. However, the reaction of trichloroacetic acid with phenylmagnesium bromide gives a mixture of diphenyl, dichloroacetic acid, phenylchloroacetic acid and diphenylacetic acid and none of the expected trichloroacetophenone.

Ketones containing one perfluoroalkyl group have been prepared by a number of routes such as: (1) the Friedel–Crafts acylation of aromatic hydrocarbons with perfluoro acid halides[3,4]; (2) the Claisen acylation of nitriles,[5] ketones[6] and esters[7] with esters of perfluorinated acids accompanied or followed by the cleavage of the β-ketonitriles, β-diketones and β-ketoesters thus formed; (3) the oxidation of secondary alcohols containing one perfluoroalkyl group[8–11]; (4) the reaction of perfluoro acid halides with organocadmium compounds,[5,6,8,12] the reactions of perfluoroalkyllithium compounds with esters[13] and[6] the reactions of Grignard reagents with perfluorinated nitriles.[14] However, all of these methods have the disadvantages that they are either of limited applicability or involve multistage syntheses.

Quite recently[15] we reported that, employing the reverse addition technique,[16] the low temperature interaction of perfluorinated acids ($C_nF_{2n+1}CO_2H$, $n = 1$–3) with phenyllithium and the room temperature interaction of the corresponding methyl esters with 2-picolyllithium give good to excellent yields of the corresponding phenyl and 2-picolyl perfluoroalkyl ketones.

We have also observed that the reaction of phenyllithium with trifluoroacetic acid[17] or perfluoropropionic acid[18] in refluxing ether gave a complex mixture of cleavage products and none of the desired phenyl perfluoroalkyl ketones. Because of the fact that organolithium compounds and Grignard reagents often give different results when treated with the same organic substrate, it was desirable to investigate the reactions of perfluorinated acids with Grignard reagents. The following reactions might occur. The perfluorinated acid may react with the Grignard, RMgX, to give the halomagnesium salt of the acid, $C_nF_{2n+1}CO_2MgX$, I, which may react with more Grignard reagent to give the dihalomagnesium salt of the dihydroxymethane, $C_nF_{2n+1}CR(OMgX)_2$, II. On loss of $(MgX)_2O$, II gives the ketone, $C_nF_{2n+1}COR$, III, which may react with more Grignard reagent to give some tertiary alcohol, $C_nF_{2n+1}COHR_2$, IV, (if the Grignard reagent has no β-hydrogen atoms) or a mixture of IV and the secondary alcohol, $C_nF_{2n+1}CHOHR$, V, (if the Grignard reagent has β-hydrogens).

Our results are given in Table I. It will be noted that in each reaction a mixture of ketone and carbinol(s) was obtained.[19] When the Grignard reagent was phenylmagnesium bromide or methylmagnesium iodide the carbinol obtained was tertiary, while with the other Grignard reagents the carbinol obtained was predominantly secondary. In all our experiments the ketone was the major product. These results are especially interesting since the reactions of perfluorinated esters with Grignard reagents containing β-hydrogen atoms give very low yields of ketones and considerably larger yields of the reduction product, the secondary alcohol.[8–11,20] Our results would seem to indicate that the addition compound II is relatively stable in the reaction mixture and that it does not decompose to any great extent to give the ketone III since, as has been demonstrated earlier,[8–11] ketones containing perfluoroalkyl groups readily undergo reduction and addition reactions when treated with Grignard reagents.

Although the above scheme requires only two moles of Grignard reagent per mole of acid to give maximum yields of ketone; when one equivalent of perfluoroacetic, propionic and n-butyric acids was treated with two equivalents of phenylmagnesium bromide in refluxing ethyl ether, the yields of the corresponding ketones were 42.5, 43 and 44.5%. However, when a 3:1 molar ratio of Grignard reagent to acid was used, these yields were increased to 58, 76 and 78%, respectively. Therefore, this latter ratio of reactants was used in all the runs in Table I. While ethyl ether was the solvent most

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[2] Part of this work was performed under Contract No. AT(30-1)-670 between the U. S. Atomic Energy Commission and the University of Pittsburgh.

[3] J. H. Simons and E. O. Ramler, THIS JOURNAL, **65**, 389 (1943).

[4] J. H. Simons, W. T. Black and R. F. Clark, *ibid.*, **75**, 5621 (1953).

[5] W. R. Nes and A. Burger, *ibid.*, **72**, 5409 (1950).

[6] L. B. Barkley and R. Levine, *ibid.*, **75**, 2059 (1953).

[7] A. L. Henne, M. S. Newman, L. L. Quill and R. A. Staniforth, *ibid.*, **69**, 1819 (1947).

[8] K. N. Campbell, J. O. Knobloch and B. K. Campbell, *ibid.*, **72**, 4380 (1950).

[9] E. T. McBee, J. F. Higgins and O. R. Pierce, *ibid.*, **74**, 1387 (1952).

[10] E. T. McBee, O. R. Pierce and J. F. Higgins, *ibid.*, **74**, 1736 (1952).

[11] E. T. McBee, O. R. Pierce and M. C. Chen, *ibid.*, **75**, 2324 (1953).

[12] R. G. Jones, *ibid.*, **70**, 143 (1948).

[13] O. R. Pierce, E. T. McBee and G. F. Judd, *ibid.*, **76**, 474 (1954).

[14] E. T. McBee, O. R. Pierce and D. D. Meyer, *ibid.*, **77**, 917 (1955).

[15] T. F. McGrath and R. Levine, *ibid.*, **77**, 3656 (1955).

[16] This technique involves the slow addition of the organometallic compound to the fluorinated compounds.

[17] T. F. McGrath and R. Levine, THIS JOURNAL, **77**, 3634 (1955).

[18] T. F. McGrath and R. Levine, *ibid.*, **77**, 4168 (1955).

[19] Similar reactions are also being studied by A. Sykes, J. C. Tatlow and C. R. Thomas. In a recent preliminary communication (*Chemistry & Industry*, 630 (1955)) they state, "From these Grignard reactions, fractions boiling higher than the ketones were obtained but as yet we have not identified them."

[20] O. R. Pierce, J. C. Siegle and E. T. McBee, THIS JOURNAL, **75**, 6324 (1953).

TABLE I

PRODUCTS FROM THE REACTIONS OF PERFLUORINATED ACIDS WITH GRIGNARD REAGENTS

Grignard[a]	Products	Yield, %	B.p. or m.p. °C.	Mm.
Acid, CF_3CO_2H				
C_6H_5	$CF_3COC_6H_5$	58	150–152	740[b,c]
	$CF_3COH(C_6H_5)_2$	6.7	74.3–75.2[b]	
n-C_3H_7	$CF_3COC_3H_7$-n	30.2, 51.2[d]	65–67	731[e]
	$CF_3CHOHC_3H_7$-n	22.7, 11.8[d]	107–108	735[f]
i-C_3H_7[d]	$CF_3COC_3H_7$-i	33.6	52–53	737[g,h]
	$CF_3CHOHC_3H_7$-i	9.7	97–100	739[i]
n-C_4H_9	$CF_3COC_4H_9$-n	52.3	91–92	741[j]
	$CF_3CHOHC_4H_9$-n	22.2	129–130	746[k]
t-C_4H_9	$CF_3COC_4H_9$-t	15.3	72–73	740[g,l]
	$CF_3CHOHC_4H_9$-t	6.4	109–112	740[m]
n-C_5H_{11}	$CF_3COC_5H_{11}$-n	69.1	76	88[n]
	$CF_3CHOHC_5H_{11}$-n	27.7	167–168	740[o]
Acid, $C_2F_5CO_2H$				
C_6H_5	$C_2F_5COC_6H_5$	76.0	159–161	740[b,p]
	$C_2F_5COH(C_6H_5)_2$	2.8	83.6–84.2[b]	
CH_3[d]	$C_2F_5COCH_3$	28.6	40	740[q,r]
C_2H_5[d]	$C_2F_5COC_2H_5$	56.5	61–62	740[s,t]
n-C_3H_7	$C_2F_5COC_3H_7$-n	28.8, 67.5[d]	82	757[u]
	$C_2F_5CHOHC_3H_7$-n	18.9, 10.8[d]	115–116	746[k]
i-C_3H_7[d]	$C_2F_5COC_3H_7$-i	42.5	73–74	737[v]
	$C_2F_5CHOHC_3H_7$-i	7.5	107–109	737[w]
n-C_4H_9	$C_2F_5COC_4H_9$-n	48.9	102–103	730[x]
	$C_2F_5CHOHC_4H_9$-n	21.5	135	746[y]
Acid, n-$C_3F_7CO_2H$				
C_6H_5	n-$C_3F_7COC_6H_5$	78	173–174	740[b,z]
	n-$C_3F_7COH(C_6H_5)_2$	7.3	116–118	4[b]
n-C_3H_7	n-$C_3F_7COC_3H_7$-n	43.8	101–102	747[aa]
	n-$C_3F_7CHOHC_3H_7$-n	8.9	130–131	741[bb]
i-C_3H_7	n-$C_3F_7COC_3H_7$-i	25.0	91–92	739[cc]
	n-$C_3F_7CHOHC_3H_7$-i	7.7	122–124	739[dd]
n-C_4H_9	n-$C_3F_7COC_4H_9$-n	53.2	121–122	748[ee]
	n-$C_3F_7CHOHC_4H_9$-n	22.6	148–149	740[ff]
			69–70	27

[a] Bromides were used to prepare all Grignard reagents except CH_3MgI and t-C_4H_9MgCl; molar ratio of Grignard reagent to acid was 3:1. [b] Melting point; see ref. 15. [c] 2,4-Dinitrophenylhydrazone, m.p. 173.0–173.6° (see ref. 15). [d] Butyl ether was used as solvent and reaction temperature was 35°; in all other runs the reactions were effected in refluxing ethyl ether. [e] 2,4-Dinitrophenylhydrazone, m.p. 75.0–75.5° (see ref. 6). [f] $n^{25}{}_D$ 1.3525 (see ref. 8). [g] See ref. 19. [h] 2,4-Dinitrophenylhydrazone, m.p. 82.0–82.6°. *Anal.* Calcd. for $C_{11}H_{11}O_4N_4F_3$: C, 41.25; H, 3.46; N, 17.50. Found: C, 41.03; H, 3.32; N, 18.13. [i] See ref. 20. [j] See H. F. Bluhm, H. V. Donn and H. D. Zook, THIS JOURNAL **77**, 4406 (1955); $n^{25}{}_D$ 1.3395; 2,4-dinitrophenylhydrazone, m.p. 48.2–48.7°. *Anal.* Calcd. for $C_{12}H_{13}O_4N_4F_3$: C, 43.15; H, 3.92; N, 16.76. Found: C, 43.30; H, 3.80; N, 16.97. [k] Behaved erratically on analysis; however, because of its b.p., there appears to be little doubt of the identity of this compound. [l] 2,4-Dinitrophenylhydrazone, m.p. 128.0–128.6°. *Anal.* Calcd. for $C_{12}H_{13}O_4N_4F_3$: C, 43.15; H, 3.92; N, 16.76. Found: C, 43.32; H, 4.03; N, 17.07. [m] See ref. 10. [n] 2,4-Dinitrophenylhydrazone, m.p. 44.6–45.2°, $n^{25}{}_D$ 1.3635 (see ref. 8). [o] $n^{25}{}_D$ 1.3828 (see ref. 8). [p] 2,4-Dinitrophenylhydrazone, m.p. 111.4–112.2° (see ref. 15). [q] 2,4-Dinitrophenylhydrazone, m.p. 100.5–101.3° (see ref. 9). [r] There was also obtained 3.5 g. of material, b.p. 84–97°, mostly at 93–97°, which is probably predominantly $C_2F_5COH(CH_3)_2$ (see ref. 9). [s] 2,4-Dinitrophenylhydrazone, m.p. 106–106.8° (see ref. 14). [t] There was also obtained 3.6 g. of material, b.p. 85–135°, which is probably a mixture of $C_2F_5CHOHC_2H_5$ (b.p. 98°) (see ref. 9) and $C_2F_5COH(C_2H_5)_2$ (b.p. 127°) (see ref. 10). [u] Behaved erratically on analysis; 2,4-dinitrophenylhydrazone, m.p. 61.5–62.1°. *Anal.* Calcd. for $C_{12}H_{11}O_4N_4F_5$: C, 38.93; H, 2.99; N, 15.13. Found: C, 39.23; H, 3.07; N, 15.33. [v] 2,4-Dinitrophenylhydrazone, m.p. 84.4–86.0°. *Anal.* Calcd. for $C_{12}H_{11}O_4N_4F_5$: C, 38.93; H, 2.99; N, 15.13. Found: C, 39.28; H, 2.83; N, 14.93. [w] See ref. 9. [x] $n^{25}{}_D$ 1.3300. *Anal.* Calcd. for $C_7H_9OF_5$: C, 41.18; H, 4.44. Found: C, 42.04; H, 4.78; semicarbazone, m.p. 91.2–91.7°. *Anal.* Calcd. for $C_8H_{12}ON_3F_5$: C, 36.78; H, 4.63; N, 16.09. Found: C, 36.71; H, 4.30; N, 16.11. [y] $n^{25}{}_D$ 1.3520. *Anal.* Calcd. for $C_7H_{11}OF_5$: C, 40.78; H, 5.38. Found: C, 41.42; H, 6.12. [z] 2,4-Dinitrophenylhydrazone, m.p. 87.0–87.9° (see ref. 15). [aa] $n^{25}{}_D$ 1.3140 (see ref. 11); 2,4-dinitrophenylhydrazone, m.p. 37.6–38.5° (see ref. 6). [bb] $n^{25}{}_D$ 1.3348 (see ref. 11). [cc] $n^{25}{}_D$ 1.3098; semicarbazone, m.p. 101.0–101.7° (see ref. 14). [dd] $n^{25}{}_D$ 1.3385 (see ref. 11). [ee] $n^{25}{}_D$ 1.3262. *Anal.* Calcd. for $C_8H_9OF_7$: C, 37.80; H, 3.57. Found: C, 37.71; H, 4.23; semicarbazone, m.p. 92.5–95.8°. *Anal.* Calcd. for $C_9H_{12}ON_3F_7$: C, 34.73; H, 3.89; N, 13.50. Found: C, 34.33; H, 3.39; N, 13.73. [ff] $n^{25}{}_D$ 1.3445. *Anal.* Calcd. for $C_8H_{11}OF_7$: C, 37.51; H, 4.33. Found: C, 37.06; H, 4.63.

often used, n-butyl ether was used in a few cases where it was difficult to separate the ketones from ethyl ether. It may be seen that when perfluoroacetic and propionic acids were treated with n-propylmagnesium bromide using both ethyl and n-butyl ether as the solvent, considerably higher yields of mixed products (*i.e.*, ketone and carbinol) were obtained with the latter solvent and simultaneously the yield of the ketone was greatly increased and that of the carbinol was greatly decreased. The reasons for this solvent effect are not apparent at present, but their implications are being investigated.

Finally, we studied the reaction of trichloroacetic acid with phenylmagnesium bromide in refluxing ether. In contrast with the results obtained above with trifluoroacetic acid, none of the expected trichloroacetophenone was obtained. Instead, a mixture[21] of biphenyl (X), dichloroacetic acid (XI), phenylchloroacetic acid (XII) and diphenylacetic acid (XIII) was obtained. This experiment shows that a carbon–chlorine bond appears to be more readily attacked by a Grignard reagent than is a carbon–fluorine bond. In this complex reaction, the trichloroacetic acid is no doubt first converted to its bromomagnesium salt VI by reaction with phenylmagnesium bromide. This salt then may undergo Grignard exchange to give VIII and chlorobenzene, which are probably the precursors of compounds X–XIII.[22]

$$\underset{\text{VI}}{CCl_3CO_2MgBr} + \underset{\text{VII}}{C_6H_5MgBr} \longrightarrow \underset{\text{VIII}}{BrMgCCl_2CO_2MgBr} + \underset{\text{IX}}{C_6H_5Cl}$$

$$\text{VII} + \text{IX} \xrightarrow{\text{Wurtz–Fittig}} \underset{\text{X}}{C_6H_5C_6H_5} + MgBrCl$$

$$\text{VIII} \xrightarrow[\text{2, } H_2O/H^+]{\substack{\text{1, } C_6H_5MgBr \\ \text{Wurtz–Fittig}}} \underset{\text{XI}}{CHCl_2CO_2H} + \underset{\text{XII}}{C_6H_5CHClCO_2H} + (C_6H_5)_2CHCO_2H \quad \text{XIII}$$

Experimental

Reaction of n-Propylmagnesium Bromide (Three Equivalents) with Trifluoroacetic Acid (One Equivalent). (A) In Refluxing Ethyl Ether.—Trifluoroacetic acid (34.2 g., 0.3 mole), dissolved in 75 ml. of anhydrous ether, was added dropwise over a two-hour period to a rapidly stirred solution

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(21) Earlier we found[17] that the reaction of trichloroacetic acid with phenyllithium in refluxing ether gave a mixture of biphenyl, benzophenone, triphenylmethane and tetraphenylethylene and none of the desired trichloroacetophenone.

(22) In this connection it is of interest to note that A. Kaluszyner and S. Reuter (THIS JOURNAL, **75**, 5126 (1953)) have treated ethyl trichloroacetate with phenylmagnesium bromide and obtained a mixture of chlorobenzene and biphenyl. These observations have been confirmed in the present study.

of *n*-propylmagnesium bromide (0.9 mole in 600 ml. of anhydrous ether). The mixture was refluxed for two hours after the addition of the acid was completed and then poured onto a mixture of ice and an excess of concentrated hydrochloric acid. The layers were separated and the aqueous phase was extracted with several portions of ether. The combined ether extracts were washed several times with a saturated sodium bicarbonate solution to remove unreacted trifluoroacetic acid and then dried over Drierite. The solvent was removed and the residue distilled to give 12.7 g. (30.2%) of 1,1,1-trifluoro-2-pentanone (b.p. 65–67° at 731 mm., 2,4-dinitrophenylhydrazone, m.p. 75.0–75.5°[6] (from ethanol–water)) and 9.7 g. (22.7%) of 1,1,1-trifluoro-2-pentanol, b.p. 107–108° at 735 mm.[8]

(B) In *n*-Butyl Ether at 35°.—When the last reaction was repeated except that the Grignard reagent was prepared in *n*-butyl ether and the reaction was effected at 35°, there was obtained a mixture of 1,1,1-trifluoro-2-pentanone (21.8 g., 51.2%) and 1,1,1-trifluoro-2-pentanol (5.0 g., 11.8%).

Reaction of Phenylmagnesium Bromide (Three Equivalents) with Trichloroacetic Acid (One Equivalent).—Trichloroacetic acid (49.0 g., 0.3 mole), dissolved in 75 ml. of anhydrous ethyl ether, was added dropwise over a period of 2.5 hours to a rapidly stirred solution of phenylmagnesium bromide (0.9 mole in 1200 ml. of ether). The mixture was refluxed for an additional two hours and then poured onto a mixture of ice and excess hydrochloric acid. The layers were separated and the aqueous phase was extracted with several portions of ether. The combined ether extracts were washed several times with saturated aqueous sodium bicarbonate solution. The bicarbonate-washed ether extracts were dried over Drierite, the solvent was removed and the residue was processed to give 28.3 g. of biphenyl (b.p. 85–95° at 2 mm., m.p. 68.5–69.5° alone and when mixed with an authentic sample) and 2.0 g. of diphenylacetic acid, m.p. 144.0–144.8° alone and when mixed with an authentic sample, amide m.p. 166.0–167.0°.[23] The sodium bicarbonate washings were acidified with hydrochloric acid, extracted several times with ether and the combined ether extracts were dried over Drierite. After removing the solvent the residue was distilled to give 14.5 g. of dichloroacetic acid (b.p. 95–96° at 18 mm., aniline salt m.p. 122.8–123.4°[24] alone and when mixed with an authentic sample) and 6.9 g. of phenylchloroacetic acid (b.p. 125–140° at 3 mm., m.p. 79.4–80.1°[25] (from 60–70° petroleum ether); amide m.p. 117.5–118.4°[25] (from benzene); alkaline hydrolysis of a sample of the phenylchloroacetic acid gave *dl*-mandelic acid, m.p. 118.7–119.0°.[26]

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[23] R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," Third Edition, John Wiley and Sons, Inc., New York, N. Y., 1948.

[24] H. W. Doughty, THIS JOURNAL, **47**, 1095 (1925).

[25] H. A. Michaël and J. Jeanpretre, *Ber.*, **25**, 1680 (1892).

[26] S. M. McElvain, "The Characterization of Organic Compounds," revised edition, The Macmillan Co., New York, N. Y., 1953.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Formation of Vicinal Dichlorides in the Reaction of Alcohols with Phosphorus Pentachloride[1]

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The reaction of phosphorus pentachloride with several secondary alcohols in chloroform at room temperature results in the formation of vicinal dichlorides together with the monochlorides. Cyclohexanol is converted to cyclohexyl chloride (50%) and *trans*-1,2-dichlorocyclohexane (28%); cyclopentanol and 3,3-dimethylcyclohexanol are similarly converted to the corresponding monochlorides and *trans*-1,2-dichlorides. Several acyclic secondary alcohols have been investigated and found to give vicinal dichlorides together with the monochlorides. The only primary alcohol investigated, *n*-octanol, is converted to *n*-octyl chloride and no evidence was obtained for the formation of a dichloride. The process by which the dichlorides are formed is stereospecific in the sense that only *trans*-vicinal dichlorides are formed from cycloalkanols and the vicinal dichloride obtained from optically active 3,3-dimethylcyclohexanol is optically active. The vicinal dichloride obtained from optically active 2-octanol has little if any optical activity. Control experiments demonstrate that the monochloride is not an intermediate in the formation of dichloride. It is proposed that the dichlorides result from a process similar to that involved in the conversion of tertiary bromides to vicinal dibromides by reaction with bromine.

Introduction

In the course of another investigation we were interested in a method for converting optically active 3,3-dimethylcyclohexanol into active 3,3-dimethylcyclohexyl chloride. Several standard methods for converting alcohols to chlorides were investigated including the method developed by Shoppee and co-workers[2] which involves the reaction of an alcohol with phosphorus pentachloride in dry chloroform at 0–25°. It has been shown[2] that under these conditions the reaction is stereospecific—the hydroxyl group is replaced by chlorine with inversion of configuration—and good yields are obtained in cases where thionyl chloride gives only unsaturated products.[2a] In the present work we have found that by this procedure optically active 3,3-dimethylcyclohexanol, $[\alpha]^{25}\text{D}$ 1.13°,[3] is indeed converted to active 3,3-dimethylcyclohexyl chloride $[\alpha]^{24}\text{D}$ −2.37°, in better yield (55%) than by any of the other methods investigated.[4] However, in addition to the 3,3-dimethylcyclohexyl chloride, considerable quantities (30%) of dichlorodimethylcyclohexane are also formed.

The formation of the dichloride was unexpected and apparently has not been observed previously under these conditions. For this reason it was of interest to investigate the reaction of various alcohols with phosphorus pentachloride in chloroform to determine if the formation of dichlorides is general.

Results

As shown in Table I all of the secondary alcohols investigated except isopropyl alcohol give appreciable quantities of 1,2-dichloride together with the monochloride as illustrated below.

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[1] This work was supported by the Research Committee of the Graduate School with funds given by the Wisconsin Alumni Research Foundation.

[2] (a) R. J. Bridgewater and C. W. Shoppee, *J. Chem. Soc.*, 1709 (1953); (b) C. W. Shoppee and G. H. R. Summers, *ibid.*, 1790 (1952).

[3] All specific rotations are for pure liquid samples.

[4] Thionyl chloride gave a maximum yield of 10%, phosphorus trichloride gave none of the desired product, and hydrochloric acid gave a 70% yield of 3,3-dimethylcyclohexyl chloride; however, the product was almost completely racemic.