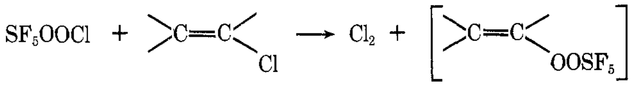
The above considerations could account for the difference in reaction of the two peroxyhypochlorites with C_2F_3Cl and CF_2CCl_2. If SF_5OOCl is less electrophilic, the selectivity and ease of addition with these olefins may decrease. If the oxygen–chlorine bond is weaker in SF_5OOCl, a side reaction of the type



may be thermodynamically and/or kinetically more favorable. Some evidence for latter was obtained by the reaction of SF_5OOCl with $CH_3C(O)Cl$. The formation of Cl_2 and $CH_3C(O)OOSF_5$[21] occurred in high yield. There is at least some similarity between the carbon–chlorine bond in -C(O)Cl and >C=C–C and we believe the above side reaction takes place to give unstable peroxides as indicated, with a concomitant decrease in yield of the addition product.

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References and Notes

(1) Alfred P. Sloan Fellow, 1975–1977.
(2) P. A. Bernstein, F. A. Hohorst, and D. D. DesMarteau, *J. Am. Chem. Soc.*, **93**, 8882 (1971).
(3) N. S. Walker and D. D. DesMarteau, *J. Am. Chem. Soc.*, **97**, 13 (1975).
(4) F. A. Hohorst and D. D. DesMarteau, *J. Inorg. Nucl. Chem.*, H. H. Hyman Memorial Issue, in press.
(5) F. A. Hohorst, J. V. Paukstelis, and D. D. DesMarteau, *J. Org. Chem.*, **39**, 1298 (1974).
(6) D. D. DesMarteau, *J. Am. Chem. Soc.*, **94**, 8933 (1972).
(7) R. M. Hammaker and D. D. DesMarteau, in preparation.
(8) A. Smith and A. W. C. Menzies, *J. Am. Chem. Soc.*, **32**, 897 (1910).
(9) P. Torkington and H. W. Thompson, *Trans. Faraday Soc.*, **41**, 236 (1945).
(10) L. R. Anderson, D. E. Young, D. E. Gould, R. Jurick-Hogen, D. Nuechterlein, and W. B. Fox, *J. Org. Chem.*, **35**, 3730 (1970); W. Maya, C. J. Shack, R. D. Wilson, and J. S. Muirhead, *Tetrahedron Lett.*, 3247 (1969).
(11) Some different, but related ethers have been obtained by reactions of SF_5OF: S. M. Williamson and G. H. Cady, *Inorg. Chem.*, **1**, 673 (1962); R. D. Place and S. M. Williamson, *J. Am. Chem. Soc.*, **90**, 2550 (1968).
(12) Private communication, W. B. Fox, Naval Research Laboratory, Washington, D.C.
(13) The ^{19}F NMR of this CF_2 group was not clearly resolved. It is a basic quintet of doublets but the lines are broadened and the pattern is asymmetric. This is not the case for the same ether derivative, and may reflect second-order effects caused by a restricted rotation about the carbon-oxygen bond in $SF_5OOCF_2CCl_3$. A similar but less pronounced effect was observed for $SF_5OOCF_2CFCl_2$ and $SF_5OOCFClCF_2Cl$. Here again, the ether derivatives showed well-resolved, symmetric patterns for the -CFCl- and -CF_2- groups.
(14) H. A. Carter and J. M. Shreeve, *Spectrochim. Acta, Part A*, **29**, 1321 (1973).
(15) See ref 10–12.
(16) C. I. Merrill and G. H. Cady, *J. Am. Chem. Soc.*, **85**, 909 (1963).
(17) W. P. Van Meter and G. H. Cady, *J. Am. Chem. Soc.*, **82**, 6005 (1960).
(18) H. J. Emeleus and K. J. Pacher, *J. Chem. Soc.*, 771 (1962).
(19) W. B. Fox and G. Franz, *Inorg. Chem.*, **5**, 946 (1966).
(20) This is recognized as being a rather tenuous argument. Some other support for a weaker O–Cl bond in SF_5OOCl comes from a comparison of the vibrational spectra of CF_3OOCl and SF_5OOCl. Reference 7 and D. D. DesMarteau and R. M. Hammaker, to be published.
(21) M. J. Hopkinson and D. D. DesMarteau, *J. Fluorine Chem.*, in press.

Pinacolyl Chloride Revisited. A Practical Synthesis

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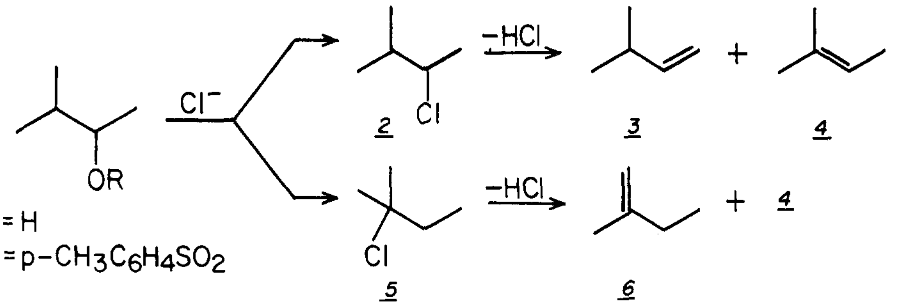
The synthesis of 3-methyl-2-chlorobutane in 90% yield and 3,3-dimethyl-2-chlorobutane (pinacolyl chloride) in 49% yield in which Wagner–Meerwein rearrangement products are completely absent is described. The method involves the displacement of the corresponding *p*-toluenesulfonyl esters with lithium chloride in dimethyl sulfoxide and hexamethylphosphoramide under moderate vacuum and temperature with concomitant evaporation of the chlorides produced. The application of several methods of halogenation to pinacolyl alcohol is discussed.

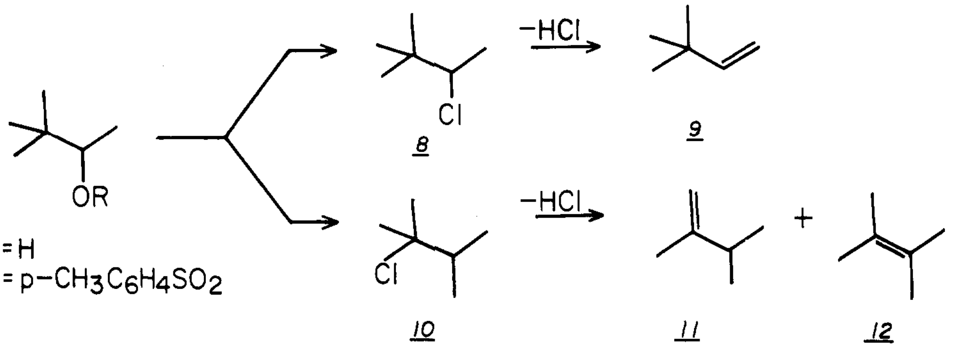
In connection with gas-phase kinetic studies pinacolyl chloride (8) was required in high purity. The tendency of this compound to rearrange under the conditions required for its synthesis is well known[1–4] and contaminants are usually difficult to separate. In fact, compound 8 and 2,3-dimethyl-2-chlorobutane (**10**), the Wagner–Meerwein rearrangement product of 8, differ in boiling point by only 1 °C.[4] The inherent steric hindrance of the secondary neopentylic carbon implies the use of rather harsh reaction conditions for bimolecular displacements to take place. Consequently significant quantities of olefins are generally produced.

These difficulties thwarted all efforts directed toward the synthesis of pinacolyl chloride until Whitmore[5] was able to obtain it by means of the chlorination of 2,2-dimethylbutane, albeit in poor yield.

Although 3,3-dimethyl-2-chlorobutane has been the subject of a limited number of studies,[3,6,28] the literature is exceedingly scant of reports about its synthesis. Addition of hydrogen chloride to 3,3-dimethylbut-1-ene[2,3] makes the task of isolation of 8 nearly impossible for practical purposes, for considerable amounts of **10** are produced. Similar results would arise from the chlorination of the corresponding hydrocarbon.[5] The halogenation of pinacolyl alcohol (**7a**) or some derivative thereof, though not devoid of obstacles, represented a more viable approach. In the present report an efficient synthesis of pinacolyl chloride free of compound **10** is described.

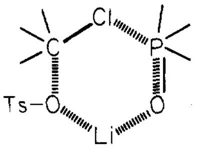
Treatment of carbinol **7a** with thionyl chloride in pyridine,[7,8] acetyl chloride, or phosphorus halides[9] furnished small quantities of 8 in admixture with several carbenium ion derived products. The use of phosphorus reagents of the triphenyl phosphite type appeared more promising. The reaction of triphenyl phosphite-benzyl chloride adduct[10] with 3-methylbutan-2-ol (**1a**), a model compound less prone to rearrange than **7a**, in dimethylformamide at room temperature gave a mixture of 2-chloro-3-methylbutane (**2**) and 2-chloro-2-methylbutane (**5**) in a 2:3 ratio. Analogously, pinacolyl alcohol yielded both chlorides 8 and **10**. This result is in consonance with the observed rearrangement during the halogenation of neopentyl alcohol.[11,12] Wiley et al.,[13] inter alia,[12] introduced the use of a





triphenyl phosphite–chlorine complex for the halogenation of alcohols and were able to obtain a 92% yield of neopentyl chloride from the carbinol without detectable rearrangement. Unfortunately, in our hands this procedure met with failure when applied to 8 under strictly anhydrous conditions. The adduct of triphenylphosphine and carbon tetrachloride has allowed for the conversion of several rearrangement-prone carbinols to chlorides under very mild conditions.[14] Snyder showed recently that treatment of an allylic alcohol with this particular reagent provided the desired allylic chloride along with 11% of rearranged halide.[15] This encouraging result, however, found no success when applied to 8 under a variety of reaction conditions.[16,17] Addition of 1 equiv of pyridine or *N,N*-dimethylaniline in an attempt to control the pH of the reaction medium inhibited halogenation.

The direct displacement of *p*-toluenesulfonic acid esters by halide ions is well documented.[18,19] This transformation is strongly dependent on the steric environment around the reaction center as illustrated by the poor yield of 2-methyl-1-bromocyclopentane obtained from the reaction of the corresponding tosylate with sodium bromide in DMF.[19] Nevertheless, moderately hindered halides like *sec*-amyl bromide have been synthesized by this method and more importantly without appreciable rearrangement.[9] Accordingly, the reaction of the model compound **1b** with chloride ion was examined. The tosylate (20 mmol) was stirred with lithium chloride (28 mmol) in dimethyl sulfoxide or DMF at room temperature under anhydrous conditions for 72 h. Moderate vacuum was applied and volatile material trapped at −78 °C furnishing a 93% yield of a colorless liquid. VPC analysis showed it to contain 96% 2-chloro-3-methylbutane (**2**), less than 1% 2-chloro-2-methylbutane (**5**), and 3% of minor impurities. Distillation of this material yielded pure compound **2**.[20] The tosylate of pinacolyl alcohol (**7b**)[21] remained unaffected under these conditions after 100 h of contact. In DMF at temperatures above 60 °C elimination became predominant.[22] In Me_2SO, in turn, substitution became significant only at 115 °C but the pinacolyl chloride produced was accompanied by copious amounts of olefinic material. The addition of hexamethylphosphoramide[23] allowed the reaction to proceed smoothly at 50 °C only furnishing compound **8** in satisfactory yield containing no detectable amounts of compound **10** and a reduced percentage of olefins. The intermediacy of the six-membered transition state **13** in which HMPA appears associated with the inorganic salt has been proposed.[24] This participation would account for the lower activation energy of the substitution reaction when HMPA is added, although other still unknown factors may be involved.



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Further studies on the gas-phase behavior of pinacolyl chloride are being conducted in our laboratory.

Experimental Section[25]

Preparation of 3,3-Dimethyl-2-chlorobutane (8). A dry 500-ml round-bottomed flask, flushed with nitrogen, and equipped with a magnetic stirrer and a 5-in. Vigreux column connected to a dry ice–acetone trap, was charged with 40 g (0.15 mol) of 3,3-dimethyl-2-butyl *p*-toluenesulfonate (**7b**),[21] 34 g (0.8 mol) of anhydrous lithium chloride, 200 ml of dry Me_2SO, and 70 ml of HMPA. The mixture was stirred at ca. 54 °C (oil bath) under 10-mm vacuum for 90 h while volatile materials were allowed to distill into the trap. Colorless liquid (14.9 g) was recovered, washed with 5% aqueous potassium bicarbonate and water, and dried briefly over magnesium sulfate. VPC analysis indicated the presence of 54% 3,3-dimethyl-2-chlorobutane (**8**, 50% yield), 19% 3,3-dimethylbut-1-ene (**9**), 14% 2,3-dimethylbut-1-ene (**11**), and 13% 2,3-dimethylbut-2-ene (**12**). The absence of compound **10** in the crude mixture was attested by the lack of a δ 1.59 ppm signal in the NMR spectrum corresponding to the *gem*-dimethyl grouping.[3,26]

Purification of 8. Purification of the chloride 8 was achieved by passing the crude material through a column of neutral alumina activity III in pentane followed by vacuum gradient distillation at a temperature not above 38 °C.[27] Pentane and the olefins were distilled at room temperature (100–50 Torr) and condensed in a cold trap. Pure pinacolyl chloride (**8**, 9.2 g, 49% yield) distilled next at 30–35 °C (oil bath) (20 Torr): ir (neat)[28] 2975 (s), 2860 (m), 1455 (m), 1375 (m), 1360 (s), 1270 (m), 1190 (m), 1070 (s), 860 (m), 725 (m), and 664 cm^{-1} (s); NMR ($CDCl_3$, 4 M) δ 1.08 (s, 9, 3 CH_3), 1.51 (d, 3, CH_3CH, $J = 7.0$ Hz), 3.83 (q, 1, methyne, $J = 7.0$ Hz); mass spectrum *m/e* (rel intensity) 107, 105 ($M^+ - 15$) (2, 6), 69 (22), 57 (100).

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Registry No.—**7b**, 25966-61-4; **8**, 5750-00-5; lithium chloride, 7447-41-8.

References and Notes

(1) F. C. Whitmore and H. S. Rothrock, *J. Am. Chem. Soc.*, **55**, 1106 (1933); F. C. Whitmore and F. Johnston, *ibid.*, **55**, 5020 (1933).
(2) G. G. Ecke, N. C. Cook, and F. C. Whitmore, *J. Am. Chem. Soc.*, **72**, 1511 (1950).
(3) H. Bilke, G. Collin, C. Duschek, W. Hoebold, R. Hoehn, W. Pritzkow, H. Schmidt, and D. Schnurpfeil, *J. Prakt. Chem.*, **311**, 1037 (1969).
(4) 2,3-Dimethyl-2-chlorobutane, bp 112 °C (749 Torr); see D. Pawlow, *Justus Liebigs Ann. Chem.*, **196**, 124 (1879). 3,3-Dimethyl-2-chlorobutane, bp 109 °C (734 Torr); see ref 5.
(5) F. C. Whitmore, H. I. Bernstein, and L. W. Mixon, *J. Am. Chem. Soc.*, **60**, 2539 (1938).
(6) J. E. Anderson and H. Pearson, *J. Chem. Soc., Chem. Commun.*, 908 (1972), and references cited therein.
(7) F. C. Whitmore and F. A. Karnatz, *J. Am. Chem. Soc.*, **60**, 2536 (1938).
(8) Previously treated with triphenyl phosphite.
(9) J. Cason and J. S. Correia, *J. Org. Chem.*, **26**, 3645 (1961).
(10) H. N. Rydon, *J. Chem. Soc.*, 2224 (1953).
(11) G. J. Karabatsos, C. E. Orzech, Jr., and S. Meyerson, *J. Am. Chem. Soc.*, **86**, 1994 (1964); R. E. Ireland, C. J. Kowalsky, J. W. Tilley, and D. M. Walba, *J. Org. Chem.*, **40**, 992 (1975).
(12) H. R. Hudson, *J. Chem. Soc. B*, 664 (1968).
(13) G. A. Wiley, B. M. Rein, R. L. Hershkowitz, and B. C. Chung, *J. Am. Chem. Soc.*, **86**, 964 (1964); G. A. Wiley, B. M. Rein, and R. L. Hershkowitz, *Tetrahedron Lett.* 2509 (1964).
(14) P. C. Crofts and I. M. Downie, *J. Chem. Soc.*, 2559 (1963); I. M. Downie, J. B. Holmes, and J. B. Lee, *Chem. Ind.* (*London*), 900 (1966).
(15) E. T. Snyder, *J. Org. Chem.*, **37**, 1466 (1972).
(16) At the time of this writing the use of solid phase phosphorus reagents for the conversion of alcohols to alkyl halides has been reported. Its behavior with compounds amenable to rearrangement remains to be explored. See S. L. Regen and D. P. Lee, *J. Org. Chem.*, **40**, 1669 (1975).
(17) After 14 h of reaction at ca. 42 °C a 90% yield of material composed of 9% olefins and 91% chlorides **8** and **10** in a 2:3 ratio was obtained.
(18) R. S. Tipson, M. A. Clapp, and L. H. Cretcher, *J. Org. Chem.*, **12**, 133 (1947); R. T. Blikenstaff and F. C. Cheng, *J. Am. Chem. Soc.*, **80**, 2726 (1958), and references cited therein.
(19) G. L. Jenkins and J. C. Kellett, Jr., *J. Org. Chem.*, **27**, 624 (1962).
(20) A. Wyschnegradsky, *Justus Liebigs Ann. Chem.*, **190**, 357 (1878).
(21) J. E. Nordlander, R. R. Gruetzmacher, and F. Miller, *Tetrahedron Lett.*, 927 (1973).
(22) Dimethylformamide is known to promote hydrogen halide elimination in alkyl halides at moderately high temperatures. See N. Kornblum and R. K. Blackwood, *J. Am. Chem. Soc.*, **78**, 4037 (1956).
(23) Lithium halides in combination with HMPA has been used in lithium salt catalyzed ring opening of glycidic esters. See B. C. Hartman and B. Rickborn, *J. Org. Chem.*, **37**, 2060 (1972).
(24) J. F. Normant and H. Deshayes, *Bull. Soc. Chim. Fr.*, 2455 (1967); H. Normant, *ibid.*, 801 (1968).
(25) 3-Methylbutan-2-ol and 3,3-dimethylbutan-2-ol were purchased from Aldrich Chemical Co. Infrared spectra were measured on a Perkin-Elmer 337 spectrophotometer. NMR spectra were obtained from a Varian Associates A-60 spectrometer using a mixture of tetramethylsilane, acetone, methylene chloride, and chloroform as internal standards. VPC analyses were performed in a Varian Aerograph series 1400 gas chromatograph using a 5% diisodecyl phthalate on Chromosorb G column treated with dimethylchlorosilane. Mass spectra were obtained from a Varian MAT 111 instrument at 20 eV. The experimental conditions described furnish a maximum yield of compound **8**.
(26) Compounds **8** and **10** have essentially the same retention time in a variety of columns.
(27) Distillation of pinacolyl chloride at atmospheric pressure was precluded by its decomposition into hydrogen chloride and olefins at temperatures above 70 °C.
(28) J. J. Shipman, V. L. Folt, and S. Krim, *Spectrochim. Acta*, **18**, 1603 (1962).

Charge-Transfer Polymers Containing 7,7,8,8-Tetracyanoquinodimethan and Tetrathiafulvalene

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Semiconducting charge-transfer polyurethanes were prepared by condensation of 2,5-bis(2-hydroxyethoxy)-7,7,8,8-tetracyanoquinodimethan with 1,1′-diisocyanatoferrocene or 4,4′-diisocyanatotetrathiafulvalene. Powder compactions of the black polymers have electrical conductivities of 3×10^{-3} and 1.66×10^{-7} ohm^{-1} cm^{-1}, respectively. Condensation of 4,4′-bis(hydroxymethyl)tetrathiafulvalene with 4,4′-diisocyanatotetrathiafulvalene gave a polyurethane which was converted to its iodide. The iodide has an electrical conductivity of 2×10^{-6} ohm^{-1} cm^{-1}. The syntheses of monomers are described.

Although many semiconducting organic polymers have been synthesized, the goal of an organic polymer having metallic conductivity has remained elusive. The recent demonstration of metallic conductivity in the charge-transfer complex of 7,7,8,8-tetracyanoquinodimethan (TCNQ) and tetrathiafulvalene (TTF)[1,2] suggested that polymers containing these materials might display metallic conductivity if properly oriented. The literature contains many examples of electrically conductive polymers in which $TCNQ\cdot^-$ is present as a counterion in a polymeric quaternary ammonium ion.[3] To prepare a polymer containing covalently bound TCNQ, it was necessary to synthesize a TCNQ derivative containing suitable reactive functional groups on the ring. The sequence of reactions used to synthesize 2,5-bis(2-hydroxyethoxy)-7,7,8,8-tetracyanoquinodimethan (**1**) is shown in eq 1.

2,5-Bis(2-hydroxyethoxy)-7,7,8,8-tetracyanoquinodimethan (**1**) is a stable red compound with mp 228–232 °C. A charge-transfer polymer was prepared by reaction of **1** with 1,1′-diisocyanatoferrocene[4] to give a black polyurethane, **2**, containing electron-acceptor TCNQ units alternating with electron-donating ferrocene units. Inasmuch as the polymer is insoluble in organic solvents, electrical conductivity measurements were performed on a compacted powder. The value obtained was 3×10^{-3} ohm^{-1} cm^{-1}, which is similar to that reported for a TCNQ complex of poly(3-vinylbisfulvalenediiron).[5]

A nonpolymeric model charge-transfer complex of 2,5-bis(2-hydroxyethoxy)-7,7,8,8-tetracyanoquinodimethan and 1,1′-bis(methoxycarbonylamino)ferrocene[4] (**3**), was prepared to compare its properties with those of the charge-transfer polymer **2**. The donor and acceptor compo-