Table I. Reaction Conditions

temp, °C	He, cm^3/min	F_2, cm^3/min	time, days
-80	60	1.0	0.5
-80	30	1.0	0.5
-80	10	1.0	0.5
-80	0	1.0	1.0
RT[a]	0	1.0	1.0
RT	0	5.0	3.0
+50	0	2.0	3.0
RT	60	0.0	1.0

[a] Room temperature.

Table II. Reaction Conditions

temp, °C	He, cm^3/min	F_2, cm^3/min	time, days
-80	60	1.0	1.0
-80	30	1.0	0.5
-80	10	1.0	0.5
-80	0	1.0	1.0
RT[a]	0	1.0	1.0
RT	0	5.0	3.0
+50	0	2.0	3.0
RT	60	0.0	1.0

[a] Room temperature.

two broad multiplets centered around +120 and +180 ppm from $CFCl_3$ which integrated for 11 and 1, respectively. Infrared analysis utilizing a KBr disk gave absorptions at 1180 (br), 1000 (m), 960 (m), 500 (w), and 480 (w) cm^{-1}. The highest molecular weight fragment observed in the mass spectrum, *m/e* 331, corresponded to the parent minus one perfluorophenyl. Freezing-point depression of bis(perfluorocyclohexyl)difluoromethane in C_6F_6 gave a molecular weight of 550 g/mol (theoretical: 612 g/mol).

Anal. Calcd for $C(C_6F_{11})_2F_2$: C, 25.5; F, 74.5. Found: C, 25.7; F, 74.1.

Discussion

The liquid range of either new compound may occur at temperatures too high for use as a blood substitute. However, as part of a multicomponent emulsion or fluorocarbon solution these perfluorocyclohexyl compounds may have utility and are currently under study. The perfluoro ring systems appear to be a favorable structural feature in fluorocarbons that dissolve oxygen[4] and it is our hypothesis that maximum oxygen solubility is obtained in fluorocarbon systems with bulky side groups which by steric bulk produce intermolecular "hole" large enough to at least partially accommodate O_2. Interestingly, the somewhat lower melting point of the tetrakis(perfluorocyclohexyl)methane may indicate more random packing in the solid state and weaker lattice interaction than in the lower molecular weight, higher melting material.

The solubility of both compounds in C_6F_6 facilitated both their purification through recrystallization and allowed a check on their molecular weights by freezing-point depression. The molecular weight of a number of fluorocarbons including perfluorohexane, perfluoromethyl- and dimethylcyclohexane, and perfluoroadamantane were determined independently with values falling within 50–75 mass units of theoretical. The complex multiplet evidenced in the CF_2 region of the ^{19}F NMR is expected in analogy with the large number of overlapping A-B systems seen in the spectrum of perfluoromethylcyclohexane. Nonetheless, integral ratios obtained for the CF_2 and CF regions were obtained consistent with the expected structure. Similarly, the broad dominant band in the C–F stretching region of the infrared is typical of that found in fluoroalkanes.

The physical appearance of tetrakis(perfluorocyclohexyl)methane is very interesting. Its appearance is like that of a clear glistening glass with some sharp edges. This physical appearance and its unusual steric bulk have made it worthwhile to attempt to grow single crystals and determine the crystal structures.[5] The rather cautious reaction conditions were chosen to produce the high yields (97% and 93%, respectively) and optimum reaction times were not considered or explored.

Perhaps the greatest significance of this work, aside from the fact that the crowded $C(C_6F_{11})_4$ compound can be prepared at all, is the fact that $C(C_6F_{11})_4$ is the first four coordinate perfluorocyclohexyl compound. As such, this work forecasts the synthesis of an unknown class of compounds, perfluorocyclohexyl organometallics [$M(C_6F_{11})_n$ when M, *n*) = (Ge, 4), (Si, 4), (Sn, 4), (W, 6), etc.], and the very interesting class of bases and stabilizing ligands [$A(C_6F_{11})_n$ when (A, *n*) = (N, 3), (P, 3), and (B, 3)].

Acknowledgment. We are grateful for the support of this work by the Air Force Office of Scientific Research (AFOSR-78-3658).

Registry No. Tetraphenylmethane, 630-76-2; tetrakis(perflurocyclohexyl)methane, 81372-16-9; diphenylmethane, 101-81-5; bis(perfluorocyclohexyl)difluoromethane, 423-06-3.

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Heterogeneous Permanganate Oxidations. 2. Oxidation of Alcohols Using Solid Hydrated Copper Permanganate[1]

N. A. Noureldin and Donald G. Lee*

Department of Chemistry, The University of Regina, Regina, Saskatchewan Canada S4S 0A2

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The heterogeneous oxidation of secondary alcohols by permanganate ion is a convenient and efficient method for the preparation of ketones.[2,3] In most of the published procedures the alcohol, dissolved in an organic solvent, is added to potassium permanganate mixed with an inert solid, and, after a certain period of stirring and/or refluxing, the product is obtained by separating and concentrating the organic solution. This approach is an improvement over traditional procedures for permanganate oxidations because of the ease with which the product may be isolated and because it can be used to selectively oxidize unsaturated alcohols without damage to the carbon–carbon double or triple bonds.[3]

Menger and Lee[4] have noted that hydration of the inert solid is essential for an efficient reaction. For example,

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(1) For part 1 of this series see ref 3.

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Table I. Hydrated Copper Permanganate Oxidations

substrate[a]	amt of oxidant, g	temp[b]	time	product (% yield)[c]
2-butanol	1.2	ambient	10 min	2-butanone (100)
2-nonanol	1.2	ambient	10 min	2-nonanone (96)
2-decanol	0.5	reflux[d]	24 h	2-decanone (80)
2-decanol	0.7	reflux[d]	24 h	2-decanone (100)
2-decanol	1.0	ambient	45 min	2-decanone (95)
2-decanol	1.2	ambient	10 min	2-decanone (92)[e]
5-decanol	1.0	ambient[d]	20 h	5-decanone (100)
5-decanol	1.2	ambient	10 min	5-decanone (84)
cyclohexanol	1.2	ambient	10 min	cyclohexanone (97)[e]
3-methylcyclohexanol	1.2	ambient	10 min	3-methylcyclohexanone (95)
norborneol	1.2	ambient	10 min	norcamphor (73)
menthol	1.2	ambient	10 min	menthone (60)
menthol	1.5	reflux[f]	1.5 h	menthone (87)
borneol	1.2	ambient	10 min	camphor (98)
benzhydrol	1.2	ambient	10 min	benzophenone (78)[g]
1-octen-3-ol	2.2	reflux[f]	48 h	1-octene-3-one (63)
1-phenyl-1-buten-3-ol	2.0	reflux[f,h]	24 h	1-phenyl-1-buten-3-one (85), benzaldehyde (10)
1-phenyl-1-penten-3-ol	2.0	reflux[f,h]	24 h	1-phenyl-1-penten-3-one (84), benzaldehyde (12)
1-phenyl-1-hexen-3-ol	2.0	reflux[f,h]	24 h	1-phenyl-1-hexen-3-one (84), benzaldehyde (9)
1-phenyl-1-butyn-3-ol	1.5	reflux[d]	30 min	1-phenyl-1-butyn-3-one (51)
1-decanol	3.0[h]	ambient	24 h	decanoic acid (81)[i]
benzyl alcohol	3.0[h]	ambient	24 h	benzoic acid (84)[i,e]
decanol	2.5	ambient	24 h	decanoic acid (91)[i]
benzaldehyde	2.5[h]	ambient	24 h	benzoic acid (99)[i,e]
di-*n*-butyl sulfide	3.0	reflux[d]	24 h	di-*n*-butyl sulfone (76)[e]

[a] 2.5 mmol of alcohol was used in each experiment. [b] Methylene chloride (10 mL) was used as the solvent. [c] Yield determined by GLC unless otherwise indicated. [d] 20 mL of solvent. [e] Isolated yields. [f] 15 mL of solvent. [g] Yield determined by NMR. [h] Copper permanganate containing 38% water was used for these experiments. In all other cases the oxidant contained 27% water. [i] The workup for acidic products included an extraction with dilute HCl/$NaHSO_3$.

they found that copper sulfate pentahydrate was superior to anhydrous copper sulfate and that "moist" molecular sieves were better than "dried" molecular sieves. They also noted that copper permanganate could be used instead of the $KMnO_4/CuSO_4$ mixture.

We have observed that a variety of other hydrated metal salts such as ferric ammonium sulfate dodecahydrate, magnesium sulfate heptahydrate, and aluminum sulfate octadecahydrate can also be successfully used as solid supports.[5] In general, the corresponding anhydrous salts are less satisfactory.

Menger and Lee[6] have also described the oxidation of several alcohols by sodium permanganate monohydrate without the aid of solid supports. In an attempt to obtain additional information which might lead to a better understanding of these important heterogeneous reactions, we have undertaken a similar study of the oxidation of alcohols by hydrated copper permanganate. In doing so we discovered what we believe to be an important synthetic procedure. Excellent yields of products (Table I) were obtained in extremely short periods of time when the alcohol, dissolved in methylene chloride, was added to hydrated copper permanganate and allowed to react for a few minutes at room temperature. However, when the hydrated copper permanganate was dried over phosphorus pentoxide before use, the yields obtained after a comparable period of time were greatly reduced (to about 3%). In addition, the vigor of the reaction was substantially lessened. When hydrated copper permanganate was used, the solvent boiled spontaneously upon addition of the alcohol solution. However, when anhydrous oxidant was used, there was no evidence of boiling.

Hydrated copper permanganate appears to give higher yields of conjugated unsaturated ketones from the corresponding allylic alcohols than does sodium permanganate monohydrate.[6] However, as previously reported for $KMnO_4/CuSO_4$ mixtures,[3] the reaction with nonallylic alcohols such as cholesterol gave little or none of the corresponding ketone; only an untractable polymeric material was obtained.

Although the mechanism of the reaction remains obscure this work has exposed a superior experimental procedure and confirmed that water is an essential component of the process.

Experimental Section

Materials. The alcohols used in this study were all obtained commercially. The hydrated copper permanganate was obtained from the Carus Chemical Co. Two batches containing different amounts of water (27% and 38%) were used with no apparent change in reactivity. Spectrograde methylene chloride (Fisher Scientific Co.) was used as the solvent without further purification.

General Procedure for the Oxidation of Secondary Alcohols. In a typical experimental procedure the reaction was initiated by addition of $Cu(MnO_4)_2 \cdot 8H_2O$ (1.2 g, 2.7 mmol) to 2-decanol (0.40 g, 2.5 mmol) dissolved in 2 mL of methylene chloride. An immediate exothermic reaction, which caused the solution to boil vigorously for about 5 min, occurred. Additional solvent (8 mL) was then added and the solution stirred at ambient temperature for 10 min. The product was separated from the inorganic residue by adding ether (10 mL), stirring for 5 min, and filtering. The inorganic residue was washed thoroughly with ether, and the combined filtrates were dried over anhydrous magnesium sulfate and concentrated on a rotary evaporator to give 0.40 g of product. Gas chromatographic analysis indicated this product to consist of only one compound, 2-decanone. Distillation [bp 78 °C (4.6 torr)] gave 0.36 g (2.3 mmol, 93%) of a product that exhibited an infrared spectrum identical with that of authentic 2-decanone.[7]

General Procedure for the Oxidation of Primary or Allylic Alcohols, Aldehydes, and Sulfides. In a typical experimental procedure, $Cu(MnO_4)_2 \cdot 8H_2O$ (3.0 g, 6.7 mmol) was added to di-*n*-butyl sulfide (0.37 g, 2.5 mmol) dissolved in 20 mL of methylene chloride. The mixture was heated under gentle reflux

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for 24 h with stirring. The mixture was then cooled to room temperature, 10 mL of ether was added, and after the mixture was stirred for another 5 min, the inorganic residue was separated by filtration through Celite. This residue was washed several times with ether, after which the filtrates were combined, dried over anhydrous magnesium sulfate, and evaporated to yield 0.37 g (2.1 mmol, 84%) of crude di-*n*-butyl sulfone, mp 35–44 °C. Recrystallization from petroleum ether (bp 30–60 °C) gave 0.34 g (1.9 mmol, 76%) of purified di-*n*-butyl sulfone [mp 42–44 °C (lit.[8] mp 43–44 °C)] which exhibited no melting point depression when mixed with an authentic sample of this compound.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada and the Carus Chemical Co. for financial assistance.

Registry No. 2-Butanol, 78-92-2; 2-nonanol, 628-99-9; 2-decanol, 1120-06-5; 5-decanol, 5205-34-5; cyclohexanol, 108-93-0; 3-methylcyclohexanol, 591-23-1; norborneol, 1632-68-4; menthol, 1490-04-6; borneol, 507-70-0; benzhydrol, 91-01-0; 1-octen-3-ol, 3391-86-4; 1-phenyl-1-buten-3-ol, 17488-65-2; 1-phenyl-1-penten-3-ol, 34862-94-7; 1-phenyl-1-hexen-3-ol, 22596-38-9; 1-phenyl-1-butyn-3-ol, 5876-76-6; 1-decanol, 112-30-1; benzyl alcohol, 100-51-6; benzaldehyde, 100-52-7; di-*n*-butyl sulfide, 544-40-1.

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Pyrido[1,2-*a*]azepines. A Correction

Gurnos Jones* and Paul Rafferty

Department of Chemistry, University of Keele, Keele, Staffordshire ST5 5BG, England

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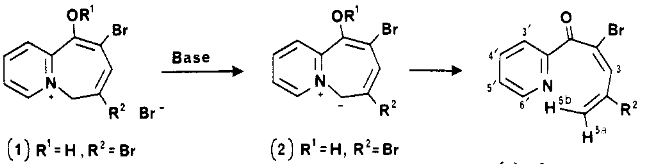
The only example of a pyrido[1,2-*a*]azepine in the literature is that reported by one of us,[1] as formed when the salt **1** was treated with aqueous base, and given the formula **2**. A renewed interest in pyridoazepines prompted us to repeat the preparation of compound **2** and submit it to ^{13}C NMR and to the higher resolving power of 100-MHz Fourier transform ^1H NMR. The ^1H NMR spectrum now reveals that the signals at δ 5.5, 5.79, and 6.92 (assigned to protons 6, 8, and the *O*H in formula **2**) are in fact a doublet, a quartet, and a doublet and that the coupling constants are 1.8 and 1.2 Hz. More crucially, the ^{13}C NMR spectrum of the compound previously formulated as **2** shows signals at δ ($CDCl_3$) 121.2 (s, C4)[3], 123.2 (s, C2), 123.6 (t, C5), 123.7 (d, C3′), 127.5 (d, C5′), 134.3 (d, C3), 137.0 (d, C4′), 149.5 (d, C6′), 151.2 (s, C2′), and 185 (s, Cl). The most notable signals are at δ 123.6 triplet in off resonance, and a carbonyl signal at δ 185. Our original IR determination in Nujol showed no strong band higher than 1620 cm^{-1}; a determination on the chloroform extract after basification of the salt **1** shows bands at 1690, 1620, and 1610 cm^{-1}. The three new pieces of evidence establish the structure of the compound as a pyridoylbutadiene **3**. Further, treatment of compound **4** (also reported in our earlier paper[1]) with cold aqueous bases gave a red, unstable compound (characterized as its picrate) whose spectral characteristics establish it as the pyridoylbutadiene **5**. Apart from the signals due to the pyridine protons, the free base **5** showed signals at δ 5.25 (1 H, d of d, J = 9 and 2 Hz, H5a), 5.4 (1 H, d of d, J = 15 and 2 Hz, H5b), 5.9–6.7 (1 H, m, H4), 7.05 (1 H, d, J = 10 Hz, H3). We have established previously that salt **1** is bicyclic, and the ^1H NMR (Me_2SO-d_6) of the salt **4** confirmed its bicyclic nature, with signals at δ 5.1 (2 H, broad, unresolved at room temperature, d of d at −40 °C, H_6), 6.1 (1 H, d of t, H7), and 6.9 (1 H, d, J = 9.5 Hz, H8). We thus assume that the pyrido[1,2-*a*]azepines **2** and **6** have only transient existence, being unstable relative to the pyridoylbutadienes **3** and **5**; we cannot rule out the possibility that traces of the pyridoazepines are present (though undetected by NMR), since the deep red color associated with compounds **3** and **5** is hard to explain on the basis of a pyridoylbutadiene chromophore. Attempts to generate the pyridoazepine **6** by treatment of salt **4** with nonnucleophilic bases in nonprotonating solvents gave red colors, but no NMR spectra could be obtained even after prolonged accumulation.



(1) R^1 = H, R^2 = Br
(4) R^1 = Ac, R^2 = H

(2) R^1 = H, R^2 = Br
(6) R^1 = R^2 = H

(3) R^2 = Br
(5) R^2 = H

Experimental Section[2]

1-Bromo-1-(2-pyridoyl)-1,3-butadiene (5). A solution of the salt **4** in the minimum of water was treated with a few drops of a saturated sodium bicarbonate solution (sodium carbonate and pyridine were also used successfully). A deep red color was produced, and extraction with dichloromethane gave, after drying and evaporation, a red oily solid. The ^1H NMR spectrum showed this to be almost pure diene **5**, characterized as its **picrate**: mp 152–154 °C; ^1H NMR ($CDCl_3$) δ 5.25 (1 H, d of d, J = 9 and 2 Hz), 5.4 (1 H, d of d, J = 15 and 2 Hz), 5.9–6.7 (1 H, m), 7.05 (1 H, d, J = 10 Hz), 7.4 (1 H, m), 7.9 (2 H, m), 8.7 (1 H, d of d, J = 4 and 1 Hz). Anal. Calcd for $C_{16}H_{11}BrN_4O_8 \cdot C_2H_5OH$: C, 42.4; H, 3.3; N, 10.9. Found: C, 42.5; H, 3.0; N, 11.15.

Registry No. 1, 1532-74-7; **3**, 81625-42-5; **4**, 1532-75-8; **5**, 81625-43-6; **5** picrate, 81625-44-7.

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(1) A. Fozard and G. Jones, *J. Org. Chem.*, **30**, 1523 (1965).

(2) NMR spectra were determined on a JEOL FX100 FT spectrometer.

(3) Off-resonance multiplicities are given in parentheses.

Synthesis of Allolaurinterol

Mohan B. Gewali and Robert C. Ronald*

Department of Chemistry, Washington State University, Pullman, Washington 99164

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Metalation of phenolic methoxymethyl ethers is an effective means of controlling the regiochemistry of substitution in complex systems and affords a convenient entry into a class of marine sesquiterpenes from *Aplysia* species and *Laurencia* species such as allolaurinterol **1**,[1] laurinterol **2**,[2] aplysin **3**,[3] and laurene **4**.[4] These com-

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