1-phenylpropane (3), based on converted 4-phenylbutanoic acid, were 35 and 5%, respectively. The nature of the product was determined on the basis of the data of the GLC MS system (Varian Mat 112 S) operating at an ionizing potential of 70 eV and an accelerating potential of 816 V (3, C_9H_{12} MS *m/e* 91 (100), 120 (22), 92 (10), 65 (9), 78 (8), 51 (5), 105 (4)). In a parallel experiment, a neutral portion was chromatographed on silica gel (pentane–ethyl ether) and the product 3 was isolated as pure product by preparative GLC from an enriched chromatographic fraction and compared (IR, NMR, MS spectra) with authentic sample. The acid fraction was treated with diazomethane in excess and analyzed by GLC as was done previously. The conversion of 4-phenylbutanoic acid was 27%. The yield of the 4-phenyl-4-acetoxybutanoic acid, based on converted 4-phenylbutanoic acid, was 16%.

(b) In the Presence of $Cu(OAc)_2$. The reaction was carried out as in (a) in the presence of 18 mmol of $Cu(OAc)_2 \cdot H_2O$. The conversion of 4-phenylbutanoic acid was 31%. The yields of lactone 2, 4-phenyl-4-acetoxybutanoic acid, and the olefins 4 and 5, based on converted 4-phenylbutanoic acid, were respectively 34, 8, 9, and 8%. The olefins 4 and 5 were isolated as was done previously by chromatography on silica gel and compared with authentic samples (4, C_9H_{10}, MS *m/e* 117 (100), 118 (80), 91 (40), 115 (25), 39 (25), 51 (17), 65 (14), 78 (10)).

Oxidation of 4-Phenylbutanoic Acid by Peroxydisulfate and $Cu(OAc)_2$. A mixture of 4-phenylbutanoic acid (20 mmol), $K_2S_2O_8$ (20 mmol), KOAc (45 mmol), and $Cu(OAc)_2 \cdot H_2O$ (10 mmol) in 50 mL of acetic acid was refluxed for 2 h. The mixture was then poured into water, separated as was done previously, and analyzed by GLC. The conversion of 4-phenylbutanoic acid was 34%. The yield of the lactone 2, 4-phenyl-4-acetoxybutanoic acid, and the olefins 4 and 5, based on converted 4-phenylbutanoic acid, was 40, 3, 15, and 6%, respectively.

Registry No. 1 (R = H), 1821-12-1; 2, 1008-76-0; 3, 103-65-1; 4, 300-57-2; 5, 103-54-8; 4-phenyl-4-acetoxybutanoic acid, 71948-82-8; $Co(OAc)_3$, 917-69-1; $Cu(OAc)_2$, 142-71-2; $K_2S_2O_8$, 7727-21-1.

Oxidation of 7-(Hydroxymethyl)bicyclo[3.3.1]nonan-3-ol. Convenient Synthesis of Bicyclo[3.3.1]nonane-3,7-dione

Julie A. Zalikowski, Kevin E. Gilbert,* and Weston Thatcher Borden

Department of Chemistry, University of Washington, Seattle, Washington 98195

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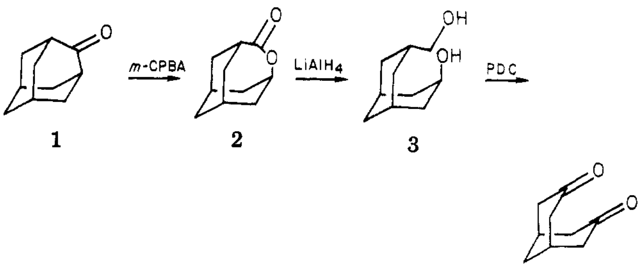
Bicyclo[3.3.*n*]alkane-3,7-diones are important intermediates in synthetic routes to alkenes containing pyramidalized carbon atoms.[1] The *n* = 1 diketone (4) can be prepared in three steps, starting from adamantane.[2] However, the second step in the sequence, the transformation of 1,3-dibromoadamantane into 7-methylenebicyclo[3.3.1]nonan-3-one, requires the use of an autoclave. The size of the autoclave available to us severely limited the amount of 4 that we could prepare in one batch; we therefore sought a more convenient route to this diketone.

Peters et al. have found that the oxidation of *endo*-7-alkyl-3-(hydroxymethyl)bicyclo[3.3.1]nonanes gives *endo*-7-alkylbicyclo[3.3.1]nonan-3-ones.[3] Although no explanation for this remarkable transformation was proposed, on the basis of this result it seemed possible that diol 3 could be oxidized directly to the diketone 4. We report herein the success of this reaction as the key step in a convenient, high-yield, three-step synthesis of 4 from the commercially available 2-adamantanone (1) (see Scheme I)

Scheme I



1 2 3

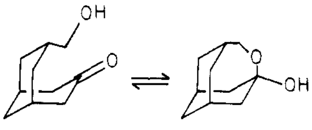
4

Oxidation of 1 with *m*-chloroperbenzoic acid gives the lactone 2,[4] which can be reduced to the diol 3 with $LiAlH_4$.[5] Although the oxidation proceeds in excellent yield (96%),[4] only a 66% yield has been reported for the reduction.[5] We have found that the diol 3 is only sparingly soluble in ether. Consequently, if hot tetrahydrofuran is used instead of ether to wash the alumina salts formed in the workup of the reduction, 3 can be isolated in nearly quantitative yield from this reaction.

After some experimentation we discovered that pyridinium dichromate (PDC)[6] oxidation of 3 for 18 h in dichloromethane provides essentially pure 4 in 75% yield. Other chromium-based reagents (Jones, Fieser, CrO_3/acetic acid, and pyridinium chlorochromate) also convert 3 to 4, but with these reagents the diketone 4 is obtained in lower yields and is accompanied by other oxidation products.

The transformation of 3 to 4 represents an apparently rare example of pyridinium dichromate in methylene chloride oxidizing a primary alcohol beyond the aldehyde stage.[6] We use a large excess of oxidizing agent, but under similar reaction conditions benzyl alcohol is only oxidized to benzaldehyde and cyclohexylmethanol to cyclohexanecarboxaldehyde.

The secondary hydroxyl in 3 is oxidized faster than the primary hydroxyl, presumably because of the greater relief of steric interactions on formation of the ketone.[7] When the reaction is terminated after 2 h, the major product is the keto alcohol 5, obtained as an equilibrium mixture in which the lactol form 6 dominates. Resubmission of this mixture to the reaction conditions for an additional 16 h gives 4.



5 6

The formation of 4 from 5 is noteworthy, since 5 lacks the endo substituent that Peters found necessary for ox-

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* To whom correspondence should be addressed at the Department of Chemistry, Indiana University, Bloomington, Indiana 47401.

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[2] A. R. Gagneux and R. Meier, *Tetrahedron Lett.*, 1365 (1969).

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[4] This reaction can be done with a number of peroxidizing reagents; see, for example, G. Mehta and P. N. Pandry, *Synthesis*, 404 (1975).

[5] H. Wynberg, A. C. Udding, and J. Strating, *Tetrahedron Lett.*, 5719 (1968). These authors report a 66% yield with no experimental data.

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[7] H. House, "Modern Synthetic Reactions", 2nd ed., W. A. Benjamin, Menlo Park, CA, 1972, p 261.

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idative loss of the hydroxymethyl group in the bicyclo[3.3.1]nonanes studied by him.[3] In these molecules and in **5** oxidative loss of the hydroxymethyl group is probably due to facile enolization of an aldehyde intermediate. Enol formation in such bicyclo[3.3.1]nonane derivatives should be favored by relief of steric crowding between bridges. Enols have been implicated in the chromic acid cleavage of ketones.[8]

Although the generation of **4** represents an unusual PDC oxidation, the success of this reaction allows the preparation of the diketone in three convenient steps and in greater than 70% overall yield. Since **4** has been utilized in the synthesis of several heteroadamantanes,[2] the convenience of our preparative method may have general utility.

Experimental Section

General Methods. Melting points are uncorrected. NMR spectra were taken on a Varian CFT-20 or EM-360L spectrometer as $CDCl_3$ solutions, and chemical shifts are reported as downfield shifts (ppm) from tetramethylsilane. Infrared spectra were taken on a Beckman Accu Lab 4. High-resolution mass spectra were obtained on an AEI MS-9 double-focusing instrument.

2-Oxatricyclo[4.3.1.1^{4,8}]undecan-9-one (2). *m*-Chloroperbenzoic acid (3.94 g, ~20 mmol, Technical Grade, 85%) was added to a solution of 2-adamantanone (3.00 g, 20.0 mmol) in dichloromethane (50 mL), and the solution was stirred at ambient temperature overnight. The solution was filtered, washed with 100 mL of 1 N NaOH, dried over $MgSO_4$, and concentrated under reduced pressure to give 3.23 g (98%) of a white solid, mp 285–287 °C (lit.[4] mp 286–288 °C).

7-(Hydroxymethyl)bicyclo[3.3.1]nonan-3-ol (3). The diol was prepared by the addition of **2** (5.44 g, 32.7 mmol) in anhydrous ether to a suspension of lithium aluminum hydride (1.24 g, 32.7 mmol) in the same solvent. After the addition was complete, the solution was refluxed for 3 h, cooled, and quenched with 1.24 mL of water, 1.24 mL of 1 N NaOH, and 3.72 mL of water. The ether phase was separated, and the alumina salts were washed with hot tetrahydrofuran (THF). The ether and THF solutions were combined, dried over $MgSO_4$, and evaporated under reduced pressure to give 5.28 g (96%) of a white solid, mp 164–165 °C (lit.[5] mp 167–168 °C).

Bicyclo[3.3.1]nonane-3,7-dione (4). The diketone was prepared by the addition of **3** (3.00 g, 17.6 mmol) in one portion to a solution of pyridinium dichromate (66.3 g, 176 mmol) in CH_2Cl_2 (160 mL) at room temperature. The solution was stirred overnight,[9] diluted with diethyl ether, filtered through a short Florisil column, dried over $MgSO_4$, and concentrated under reduced pressure to give 2.03 g (75%) of diketone, mp 250 °C (lit.[2] mp 252 °C), with spectral properties identical with those of an authentic sample.[2] This reaction could also be conveniently carried out on 10 g of diol **3**, and on this scale too a 75% yield of diketone **4** was obtained.

7-(Hydroxymethyl)bicyclo[3.3.1]nonan-3-one (5). The diol **3** (0.500 g, 2.94 mmol) was added to a solution of pyridinium dichromate (5.08 g, 13.5 mmol) in 35 mL of CH_2Cl_2. After being stirred for 2 h, the solution was diluted with ether, filtered through a short Florisil column, dried over $MgSO_4$, and evaporated under reduced pressure to give 0.404 g of product. This material was purified by chromatography on a column of neutral alumina, which was eluted with a 60:40 mixture of ethyl acetate–chloroform, yielding 0.240 g (50%) of a mixture of hydroxy ketone **5** and lactol **6**; mp 88–92 °C. The ^1H NMR spectrum ($CDCl_3$) of the mixture showed δ 1.45 (br s, 2 H), 1.87 (m, 10 H), 2.30 (br s, ~1 H), 2.70 (s, 1 H, exchangeable in D_2O), 3.27 (d, 0.4 H, J = 7 Hz), and 3.75 (d, 1.6 H, J = 3 Hz). On addition of a crystal of oxalic acid to the solution to accelerate the interconversion of **5** and **6**, the resonance at δ 2.30, ascribed to the protons α to the carbonyl in **5**, moved upfield so that it became part of the broad singlet centered at δ 1.87. In addition, the doublets at δ 3.27 and 3.75, assigned to the protons of the hydroxymethyl group in, respectively, **5** and **6**, merged to a broad 2-H singlet at δ 3.67. The ^{13}C spectrum ($CDCl_3$) of the mixture of **5** and **6** showed δ 26.84, 28.31, 28.83, 30.94, 31.69, 33.64, 34.69, 36.17, 43.98, 50.07, 67.69, 71.17, and 100.84. No attempt was made to locate the very small resonance expected for the carbonyl carbon in **5**. The IR spectrum (CH_2Cl_2) showed an OH signal at 3400 cm^{-1} and a relatively weak C=O signal at 1725 cm^{-1}.

Exact mass calcd for $C_{10}H_{16}O_2$: *m/e* 168.1149. Found: *m/e* 168.1154.

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Registry No. 1, 700-58-3; **2**, 21898-84-0; **3**, 66674-81-5; **4**, 770-15-0; **5**, 72036-39-6; **6**, 72036-40-9.

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[9] With some batches of PDC it proved necessary to reflux the reaction mixture overnight in order to complete the reaction. The results of the control experiments involving the oxidation of benzyl alcohol and cyclohexylmethanol were not affected by this change in reaction conditions.

Preparation of α,ω-Diiodoperfluoroalkanes[1]

Clifford D. Bedford and Kurt Baum*

Fluorochem, Inc., Azusa, California 91702

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Although perfluoroalkyl iodides are widely used reagents for the synthesis of fluorinated compounds, α,ω-diiodoperfluoroalkanes have not been readily accessible. A direct route to these materials by the telomerization of tetrafluoroethylene with iodine was reported by Haszeldine in 1951, but experimental details and product characterizations were not given.[2] Subsequently, Knunyants et al. attempted to repeat this work but obtained only very low yields of a mixture of telomers.[3] Although catalysts for the reaction were reported in the patent literature,[4] this direct method has not appeared to be useful for laboratory-scale preparations, and other routes have been developed. A hot-tube reaction of diacid chlorides with potassium iodide has been reported to give α,ω-diiodoperfluoroalkanes, but the preparation of the starting materials required several steps.[5] Milligram quantities of several of the diiodides were obtained by the photolysis of bromoiododifluoromethane with tetrafluoroethylene.[6]

We wish to report the development of a convenient and reproducible laboratory-scale telomerization of tetrafluoroethylene with iodine. The results of exploratory experiments are summarized in Table I. The reactions were carried out in stainless-steel cylinders at 200–220 °C and an initial pressure of 20–27 atm. No catalysts were used.

Either iodine or 1,2-diiodotetrafluoroethane can be used interchangeably as the telogen as is seen by the similarity of the results of runs 1 and 3 of Table I, which contained equivalent amounts of starting materials. Free iodine was

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[1] This work was supported by the Office of Naval Research.

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