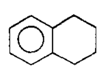
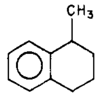
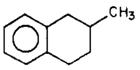
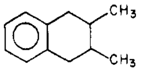
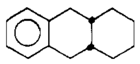
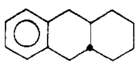
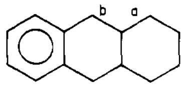
Table I. Relative Yield (%)[a] of Products of Alkyltetralin Pyrolysis

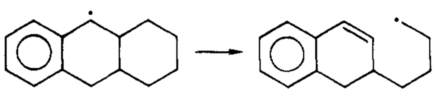
	reactant											
	 **1**		 **7**		 **8**		 **9**[b]		 **10**		 **11**	
temp, °C	737	888	732	891	797	890	737	888	758	860	752	854
benzocyclobutene (**2**)	6	6			7	5	8	4	24	15	trace	5
styrene (**3**)	10	23	4	2	5	15	trace	19	trace	19	trace	8
indene (**4**)	5	15	6	13	7	10	4	7	trace	3	trace	4
1,2-dihydronaphthalene (**5**)	55	5	26	6	18	4	trace	1				
naphthalene (**6**)	10	31	29	67	35	41	29	42	14	14	25	24
1-methylnaphthalene (**12**)		trace	3	1	1	1	3	2	1	3	5	6
2-methylnaphthalene (**13**)		trace	5	1	5	2	31	10	11	16	16	21
Σ minor products	13	20	27	10	22	22	25	15	44[c]	30[d]	48[e]	32[f]
% conversion[g]	6	89	60	99	30	84	12	95	18	78	17	67
Σ recovered material[g]	103	77	95	87	98	88	95	77	94[h]	86[i]	95[j]	87[k]

[a] Relative yield X = (absolute yield X)/(Σ all products). Absolute yields are averages of two GLC runs against an internal standard. FID response factors were determined for the major products and estimated for the minor ones. [b] This was an 80:20 trans-cis mixture. [c] Includes 10% 2-ethylnaphthalene (**14**) and 4% 2-vinylnaphthalene (**15**). [d] Includes 5% **14** and 4% **15**. [e] Includes 14% **14** and 6% **15**. [f] Includes 5% **14** and 5% **15**. [g] Absolute yield (%). [h] Includes 1% **11**. [i] Includes 4% **11**. [j] Includes 2% **10**. [k] Includes 4% **10**.

Loss of the four-carbon unit from **10** and **11** to give **6** probably does not involve initial cleavage of C–C bond a since cleavage of C–C bond b would be expected to be more favorable. The entropy changes of both reactions are similar but the enthalpy changes favor cleavage of bond b which produces the more stable benzyl radical. Thus initial loss of a benzylic hydrogen atom to form **17** would seem more likely. Loss of C_1–C_4 fragments from **18** would lead to **6**, **13**, and 2-ethyl- (**14**) and 2-vinylnaphthalene (**15**).



10 or 11



17 **18**

A concerted loss of cyclohexene readily explains the marked difference in the importance of the retro-Diels–Alder reaction for **10** and **11** since **11** would have to produce the high energy *trans*-cyclohexene.[11] However, the two-step mechanism cannot be rigorously excluded since stability or conformational differences of **10** and **11** could explain the difference in the importance of the retro-Diels–Alder reaction. Also, the two-step mechanism probably becomes important at higher temperatures and accounts for the production of **2** and **3** from **11** at 850 °C.

As a comparison to the 2-alkyltetralins, 1-methyltetralin (**7**) was pyrolyzed. The predominant product was **6**, presumably formed by direct cleavage of the benzylic methyl group. This cleavage occurs readily as evidenced by the fact that at 800 °C 90% of **7** but only 30% of **8** was converted to products.

There have been scattered reports of the thermal, gas-phase cleavage of alkyl groups,[12] but all involve the cleavage of methyl groups attached to benzylic or quaternary centers in contrast to the cleavages reported in this manuscript.

Acknowledgment. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division, Budget Code AK-01-03-021 under Contract W-7405-ENG-82.

Registry No. 1, 119-64-2; **2**, 694-87-1; **3**, 100-42-5; **4**, 95-13-6; **5**, 447-53-0; **6**, 91-20-3; **7**, 1559-81-5; **8**, 3877-19-8; *cis*-**9**, 10074-96-1; *trans*-**9**, 10074-97-2; **10**, 64363-88-8; **11**, 77341-12-9; **12**, 90-12-0; **13**, 91-57-6; **14**, 939-27-5; **15**, 827-54-3; *cis*-1,2,3,4,4a,9a-hexahydro-9-(10*H*)-anthracenone, 72036-02-3; *trans*-1,2,3,4,4a,9a-hexahydro-9-(10*H*)-anthracenone, 3586-86-5.

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Received January 22, 1981

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(11) Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Verlag Chemie GmbH: Weinheim, 1971; pp 103.

(12) (a) Brown, R. F. C.; Gream, G. E.; Peters, D. E.; Solly, R. K. *Aust. J. Chem.* **1968**, *21*, 2223. (b) Baron, W. J.; DeCamp, M. R. *Tetrahedron Lett.* **1973**, 4225. (c) Kaufmann, St.; Pataki, J.; Rosenkranz, G.; Romo, J.; Djerassi, C. *J. Am. Chem. Soc.* **1950**, *72*, 4531.

Direct One-Step Conversion of Alcohols into Nitriles[1]

Summary: Alcohols are converted into nitriles in good to excellent yields by treatment with 2 equiv of NaCN/Me_3SiCl and a catalytic amount of NaI in DMF/CH_3CN.

Sir: The conversion of alcohols into nitriles is a useful and often employed synthetic reaction sequence. It is frequently used to obtain the homologous carboxylic acid by hydrolysis of the resulting nitrile as well as the homologous amine or aldehyde by reduction. The classical methods for alcohol to nitrile conversion proceed via sulfonate ester and/or halide intermediates (Scheme I). The nucleophilic displacement of OSO_2R' by cyanide or halide is often accompanied by the undesirable side reaction of elimination to produce olefins. Other newer methods utilize various phosphorus[2] and boron[3] derivatives as intermediates to

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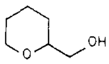
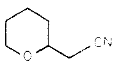
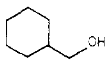
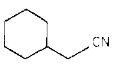
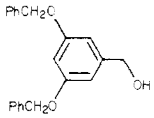
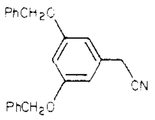
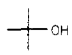
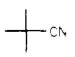
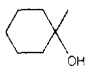
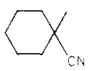
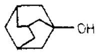
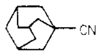
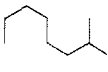
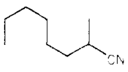
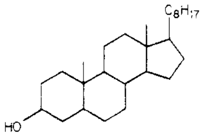
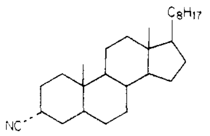
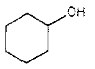
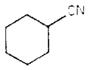
(1) Publication No. 573 from the Institute of Organic Chemistry.

(2) (a) Landauer, S. R.; Rydon, H. N. *J. Chem. Soc.* **1953**, 2221. (b) Verheyden, J. P. H.; Moffatt, J. G. *J. Am. Chem. Soc.* **1964**, *86*, 2093; *J. Org. Chem.* **1970**, *35*, 2319, 2868. (c) Lorenz, J.; Auer, J. *Angew. Chem.* **1965**, *77*, 218. (d) Rydon, H. N. *Org. Synth.* **1971**, *51*, 44. (e) Coe, D. G.; Landauer, S. R.; Rydon, H. N. *J. Chem. Soc.* **1954**, 2281. (f) Corey, E. J.; Anderson, J. E. *J. Org. Chem.* **1967**, *32*, 4160.

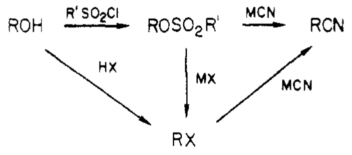
0022-3263/81/1946-2985$01.25/0 © 1981 American Chemical Society

Table I.[a] **Conversion of Alcohols into Nitriles**

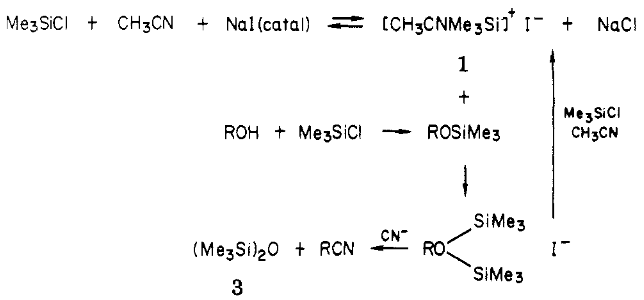
entry	alcohol	nitrile	time, h	yield,[b] %
1	$PhCH_2OH$	$PhCH_2CN$	2	98
2			2.5	98
3			4	93
4			3	98
5			5	64[c]
6			5	80
7			6	91
8			8	75
9			5	85[d]
10			8	16[e,f]

[a] Reactions were conducted in CH_3CN/DMF (1:1 v/v) at 60-65 °C under argon. [b] Yields are based on isolated products. [c] Distilled yield. *N-tert*-Butylacetamide (ca. 10%) was also isolated. [d] $[\alpha]^{25}{}_D$ +20.3° (*c* 0.8) (lit.[11] $[\alpha]^{25}{}_D$ +21°); mp 166-168 °C (lit.[12] mp 167-169 °C). Cholest-2-ene (ca. 6%) was also isolated; mp 68-70 °C (lit.[11] mp 66-68 °C). This same conversion is reported to give a 25% yield with Ph_3P-diethyl azodicarboxylate.[4] [e] *N*-Cyclohexylacetamide (73%) was isolated. [f] Satisfactory IR, ^{1}H NMR, and elemental analyses (±0.4% for C, H, and N) were obtained for the three nitriles (entries 2, 4, and 8). Nitriles of entries 1, 3, and 7 were compared directly to authentic samples (GC and/or TLC). Nitriles of entries 5, 6, and 10 and *N*-cyclohexylacetamide and *N-tert*-butylacetamide were characterized by comparing IR or NMR spectra or melting or boiling points with those published for authentic samples.

Scheme I



Scheme II



obtain alkyl iodides. A direct method for converting a secondary alcohol into a nitrile by using triphenylphosphine–diethyl azodicarboxylate has been reported,[4] but the yield of nitrile is low (25%) in this reaction compared to those for other nucleophiles studied. We report here a simple, inexpensive, direct, one-step method for the conversion of alcohols into nitriles.

Recently organosilicon reagents have been employed to good advantage in organic synthesis. One of these is trimethylsilyl iodide (Me_3SiI), the chemistry of which has been investigated and developed independently by Jung and by Olah for cleavage of esters,[5] ethers,[6] and carbamates[7] and for conversion of alcohols into iodides.[8,9] Olah and co-workers[9] have shown that this latter transformation, alcohols to iodides, proceeds to give excellent yields via a conveniently in situ generated Me_3SiI reagent from Me_3SiCl/NaI in acetonitrile. Consideration of plausible mechanisms for this transformation suggested that a similar direct conversion of alcohols into nitriles might be possible.

Our initial attempt was simply to replace the NaI of the in situ Me_3SiI reagent with NaCN and add DMF (50% v/v) for better solubility of cyanide. When benzyl alcohol is treated with Me_3SiCl (2 equiv) and NaCN (2 equiv) in DMF/CH_3CN (50/50 v/v) at room temperature or at 60 °C, no benzyl cyanide is produced. However, when a *catalytic* amount of NaI is added, a nearly quantitative yield of benzyl cyanide is realized. Our rationale for adding

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(3) (a) Freeguard, G. F.; Long, L. H. *Chem. Ind. (London)* **1964**, 1582. (b) Long, L. H.; Freeguard, G. F. *Ibid.* **1965**, 223.

(4) Loibner, H.; Zbiral, E. *Helv. Chim. Acta* **1976**, *59*, 2100.

(5) (a) Ho, T. L.; Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 774; *Synthesis* **1977**, 417; *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 4. (b) Jung, M. E.; Lyster, M. A. *J. Am. Chem. Soc.* **1977**, *99*, 968.

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(7) Jung, M. E.; Lyster, M. A. *J. Chem. Soc., Chem. Commun.* **1978**, 315.

(8) Jung, M. E.; Ornstein, P. L. *Tetrahedron Lett.* **1977**, 2659.

(9) Olah, G. A.; Narang, S. C.; Gupta, B. G. B.; Malhaltra, R. *Synthesis* **1979**, *44*, 1247 and ref 16–18 therein.

a catalytic amount of NaI was based on our postulated mechanism, which involves initial formation of the trimethylsilyl ether of the alcohol and generation of the complex formed between CH_3CN and Me_3SiI that Olah[10] has demonstrated, as depicted in Scheme II. In this way a continual amount of an electrophilic reagent, either the complex **1** or perhaps Me_3SiI, would be available for attack on the silyl ether to provide the oxonium ion **2**, which then would react with the nucleophilic and more abundant cyanide ion either by an S_N2 or S_N1 process.

The results of the conversion of a series of alcohols into the corresponding nitriles by this new method are shown in Table I. These data allow the following conclusions to be made: (a) primary, secondary, and tertiary alcohols are all converted into the corresponding nitriles in good to excellent yields; (b) the reaction proceeds with inversion of configuration as evidenced by the conversion of 3β-cholestanol into the less thermodynamically stable 3α-cyano-5α-cholestane (see entry 9); (c) the reaction, however, can proceed by an S_N1 process for a different secondary alcohol as shown by the 73% yield of *N*-cyclohexylacetamide isolated in the case of cyclohexanol (entry 10).[11] Other experiments carried out in order to elucidate the mechanism of this conversion included the following: (a) varying the stoichiometry of the in situ reagent; use of tetrahydropyranylmethyl alcohol and 1.0 equiv each of Me_3SiCl and NaCN gave a 23% yield of the corresponding nitrile, 1.5 equiv of each gave a 50% yield, and 2.0 equiv gave a 98% yield; (b) deletion of either of the two cosolvents; use of benzyl alcohol and only CH_3CN resulted in a 10% yield of benzyl cyanide in 3 h (this reaction proceeded cleanly with longer time); with the use of only DMF no reaction occurred in 3 h, but the addition of 2.5 equiv of CH_3CN at this point gave a >95% yield of nitrile in an additional 2 h; use of DMF and 2.2 equiv of CH_3CN initially gave an ≥95% yield; (c) preforming a silyl ether; the trimethylsilyl ether of benzyl alcohol was treated with Me_3SiCl/NaCN (1 equiv each) in DMF/CH_3CN (50/50 v/v) and a catalytic amount of NaI gave a 95% yield of benzyl cyanide. Finally, hexamethyldisiloxane (**3**) is the silicon-containing byproduct of this conversion. It was shown to be present in the reaction mixture and in approximately the amount expected by GC comparisons with an authentic sample.

In a typical procedure, a mixture of the alcohol (1.0 g), NaCN (2 equiv), NaI (2–5 mg), CH_3CN (10 mL), and DMF (10 mL) is deaerated, and, under an argon atmosphere, Me_3SiCl (2 equiv) is added at room temperature. The mixture is then placed in a preheated (60–65 °C) oil bath and heated with stirring for 2–8 h (the reaction is monitored by GC or TLC). When reaction is complete, the mixture is poured into H_2O (100 mL) and the mixture extracted with hexane or diethyl ether (100 mL). The organic phase is washed with H_2O (1 × 50 mL if hexane, 5 × 50 mL if ether) and with brine (50 mL), dried ($MgSO_4$), and concentrated in vacuo. In all but two reactions (*tert*-butyl alcohol and cholestanol) the nitrile thus obtained required no further purification. When necessary, the product was either distilled or recrystallized.

This alcohol into nitrile conversion because of its ease and exceptionally mild conditions promises to be general and applicable to multifunctional and sensitive substrate molecules. Further investigations into the utility of this catalytic NaI in situ generated reagent for synthetic transformations are continuing.

Acknowledgment. We thank Mrs. V. Arrizon-Lopez, Mrs. L. Kurz, and Mrs. J. Nelson for their assistance with analytical measurements and Dr. M. Marx for helpful discussions.

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[10] See footnote 15 of ref 8.

[11] Cyclohexanol represents a most difficult case for S_N2 displacement reactions. See: Henbest, H. B.; Jackson, W. R. *J. Chem. Soc.* **1962**, 954 and ref 5b therein.

[12] Roberts, G.; Shoppee, C. W.; Stephenson, R. J. *J. Chem. Soc.* **1954**, 2713.

30-Nor-3β-methoxyserrat-14-en-21-one: First Reported Natural Occurrence of a Norserratene Triterpene

Summary: A triterpenoid isolated from white pine bark (*Pinus monticola* Dongl.) has been shown to be 30-nor-3β-methoxyserrat-14-en-21-one by a combination of spectral, mass spectral, and X-ray crystallographic methods.

Sir: Serratenes are a novel group of naturally occurring pentacyclic triterpenes in which the central C ring is seven membered. In addition, all the known examples have seven tertiary methyls, one of which may occur as a hydroxymethyl, and usually have oxygen functionalities at either or both C-3 and C-21. Serratene triterpenes have been reported in such diverse plants as conifers (especially the Pinaceae)[1] and club mosses (*Lycopodium* species).[1,2]

Following a preliminary investigation of the chemistry of western white pine (*Pinus monticola* Dougl.) bark,[3] a detailed analysis of the benzene extract was conducted to determine its chemical composition.[4] During the course of that investigation, several unknown triterpenes were isolated. A number of these triterpenes had spectral properties that suggested they were serratenes.

One of the compounds (compound H—0.2% of benzene extract)[4] gave an elemental analysis (C, 81.94; H, 11.26) and molecular ion in the high-resolution mass spectrum (M^+ *m/e* 440.3674) that corresponded to an empirical formula of $C_{30}H_{48}O_2$ (calcd: C, 81.76; H, 10.98; M^+ *m/e* 440.3654). This compound has now been shown to have the structure 30-nor-3β-methoxyserrat-14-en-21-one (I) by single-crystal X-ray diffraction. Compound I is of interest because it is the first example of a naturally occurring norserratene. The full mass spectrum is consistent with the X-ray structure.

Single crystals of 30-nor-3β-methoxyserrat-14-en-21-one suitable for X-ray crystallographic data collection were obtained from methylene chloride by slow evaporation of the solvent. This compound crystallizes in the orthorhombic space group $P2_12_12_1$ with unit cell dimensions a = 9.598 (1), b = 10.559 (1), and c = 25.150 (2) Å. A total of 2414 unique reflections up to a 2θ limit of 127.5° were collected on a Picker FACS 1 diffractometer in the Biochemistry Department, University of Wisconsin—Madison, using Ni-filtered Cu Kα radiation. The structure was solved by a combination of direct and Fourier methods. After preliminary least-squares refinement of all the

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[1] Kulshreshtha, M. J.; Kulshreshtha, D. K.; Rastogi, R. P. *Phytochemistry* **1972**, *11*, 2369.

[2] Pant, P.; Rastogi, R. P. *Phytochemistry* **1979**, *18*, 1095.

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[4] Conner, A. H.; Nagasampagi, B. A.; Rowe, J. W. *Phytochemistry* **1980**, *19*, 1121.

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