**6a**, 99112-46-6; **6b**, 56100-20-0; **6b**·picrate, 56100-21-1; **6c**, 99127-91-0; 7, 99112-47-7; **8**, 99112-48-8; **10a**, 99112-49-9; **10b**, 99112-50-2; **11**, 99112-51-3; **12**, 51507-09-6; **13**, 99112-52-4; $CS_2$, 75-15-0; $H_3CI$, 74-88-4; $EtOCOC(C_6H_5){=}C(SCH_3)_2$, 5841-53-2; $C_6H_5CH_2CO_2Et$, 101-97-3; $H_3CBr$, 74-83-9; $EtOCOCH{=}C(SCH)_2$, 19606-92-9; $H_3CCO_2Et$, 141-78-6; $(H_3C)_3COCOCH{=}C(SCH_3)_2$, 99112-53-5; 2-acetylpyridine, 1122-62-9.

## Observations Regarding δ- and ε-Cyano Radical Cyclizations

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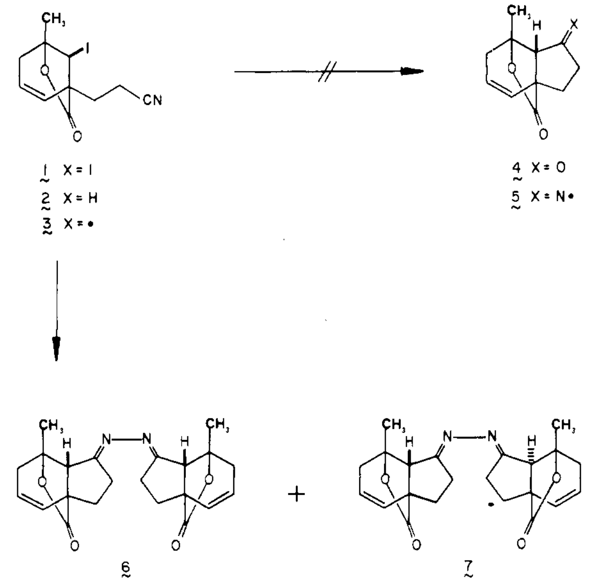
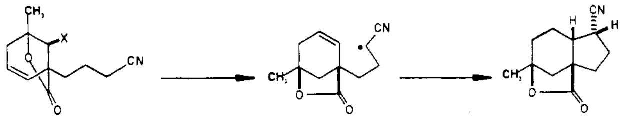
A number of intramolecular free radical additions to nitriles have been reported.[2-4] For example, such reactions have seen limited use in cyclopentanone[3] and cyclohexanone[4] synthesis. This note presents several observations which further define the scope and limitations of this free-radical-cyclization approach to cycloalkanones.

During the course of a synthetic project, we had reason to attempt the free-radical cyclization of δ-iodo nitrile 1. Treatment of a benzene solution of 1[5] with tri-*n*-butyltin hydride[6] and a catalytic amount of AIBN under high-dilution conditions at reflux gave none of the desired cyclopentanone 4. Only nitrile 2, derived from reduction of radical 3, was isolated in 95% yield. In an attempt to generate 3 in the absence of hydrogen atom donors, we turned to hexaalkyldistannanes as a source of trialkylstannyl radicals. Such a ploy has previously been used to generate free radicals for use in fragmentation[7] and intermolecular coupling[8] reactions. Thus, a benzene solution of 1 and hexamethyldistannane[9] was irradiated through Pyrex with a 450 W Hanovia medium-pressure lamp for 52 h to afford two isomeric products along with 42% of recovered 1. The products gave spectral data which were consistent with structures 6 (16%) and 7 (10%), resulting from dimerization of iminyl radical 5. The structure of 7 was ultimately established by X-ray crystallography.[10]


1 X = I
2 X = H
3 X = •
4 X = O
5 X = N•
6
7

This result indicates that the strategy for generating 3 under conditions where cyclization can compete with intermolecular processes is successful, although not outstanding from an operational standpoint.

Cyclization of iodo nitrile 8 was also examined. Treatment of a benzene solution of 8 with tri-*n*-butyltin hydride and AIBN under reflux gave lactone 10 (71%) and perhydroindan 12 (13%). The gross structures of 10 and 12 were consistent with spectral data, and the stereochemistry of 12 was established by X-ray crystallography.[10] It is clear that reduction (9 → 10) and rearrangement (9 → 11) of the initially formed radical compete with cyclization and ultimate cycloalkanone formation.[11] The rearrangement is noteworthy and perhaps explains the paucity of examples of cyclohexanone synthesis via ε-cyano


8 X = I
9 X = •
10 X = H
11
12

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† Alfred P. Sloan Foundation Fellow, 1983–1987.

[1] Author to whom inquiries regarding crystallographic studies should be addressed.

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[5] Iodo lactones 1 and 8 were prepared via reductive alkylation of *m*-toluic acid with the appropriate bromo nitriles followed by iodo lactonization of the resulting dihydrobenzoic acids. The overall yields of 1 and 8 were 78% and 76%, respectively. For similar sequences see: Chuang, C.-P.; Hart, D. J. *J. Org. Chem.* **1983**, *49*, 1782.

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[8] Stork, G.; Sher, P. M. *J. Am. Chem. Soc.* **1983**, *105*, 6765.

[9] Hexamethyldistannane was prepared using the procedure of Smith, G. F.; Kuivila, H. G.; Simon, R.; Sultan, L. *J. Am. Chem. Soc.* **1981**, *103*, 833. For other uses of hexamethyldistannane see: Krusic, P. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1971**, *93*, 846. Irradiation of 1 in the absence of hexamethyldistannane gave no reaction.

[10] Both diffraction data of compounds 7 and 12 were collected on an Enraf-Nonius CAD4 diffractometer at room temperature. Both data were corrected for Lorenz and polarization effects. All crystallographic computations were carried out on a PDP 11/44 computer using SDP (Structure Determination Package) of B. A. Frenz and Associates, Inc., which was obtained from Enraf-Nonius. Structures were solved by a combination of direct methods and difference Fourier syntheses. Colorless crystals of compound 7 crystallize in space group $p2_1/C$ with $Z = 4$ in a cell dimensions $a = 10.965$ (3) Å, $b = 11.556$ (2) Å, $c = 15.221$ (3) Å, $\beta = 95.80$ (2)°, $V = 1917.96$ Å$^3$: $R_F = 0.037$ and $R_{wF} = 0.046$ with 350 variable parameters for 1352 reflections [$I > 3.0\sigma(I)$ of 2500 symmetry-independent reflections collected in the range of $4° < 2\theta < 50°$]. Colorless crystals of compound 12 crystallize in space group $P\bar{1}$ with $Z = 4$ in a cell dimensions $a = 7.760$ (1) Å, $b = 19.993$ (2) Å, $c = 7.125$ (2) Å, $\alpha = 91.18$ (1)°, $\beta = 98.17$ (3)°, $\gamma = 83.45$ (1)° and $V = 1087.04$ Å$^3$. $R_F = 0.030$ and $R_{wF} = 0.036$ with 392 variable parameters for 2245 reflections [$I > 3.0\sigma(I)$ of 3078 unique reflections collected in the range of $4° < 2\theta < 48°$]. Complete crystallographic data appear in the supplementary material.

[11] Reduction of 8 with tri-*n*-butyltin deuteride showed that 10 was derived predominantly, if not exclusively, from reduction of radical 9 rather than 11 based on 500-MHz $^1H$ NMR analysis.

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radical cyclizations.[12] At least, this result serves as a cautionary note to those intending to incorporate such cyano radical cyclizations in projected syntheses.

## Experimental Section

All melting points are uncorrected. $^1$H nuclear magnetic resonance spectra were recorded on Varian EM-390 or Bruker AM-500 instruments and are reported in parts per million from internal tetramethylsilane on the $\delta$ scale. Data are reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants, integration, interpretation]. $^{13}$C magnetic resonance spectra were recorded on a Bruker WP-80 instrument and are recorded in parts per million from internal tetramethylsilane: chemical shift (multiplicity). Infrared spectra were recorded using a Perkin-Elmer 457 spectrometer. Mass spectra were recorded using a Kratos MS-30. The parent ions of some compounds were not observed. In these cases, fragmentation patterns were in accord with the assigned structures. Combustion analyses were performed by Micro-Analysis, Inc., Wilmington, DE.

Solvents and reagents were purified prior to use. All reactions were carried out under a blanket of nitrogen or argon in flame-dried flasks unless stated otherwise. Column chromatography was peformed over EM Laboratories silica gel (70–230 mesh) or LoBar columns (medium pressure).

***rel*-(1*S*,5*S*)-1-(2-Cyanoethyl)-5-methyl-6-oxabicyclo[3.2.1]oct-2-en-7-one (2).** To a solution of 1.08 g (3.39 mmol) of iodo nitrile 1[5] in 50 mL of dry benzene under reflux was added a solution of 1.83 g (6.3 mmol) of tri-*n*-butyltin hydride[6] and 20 mg of azo(bisisobutyronitrile) (AIBN) in 15 mL of dry benzene via syringe pump at a rate of 1.7 mL h$^{-1}$. The mixture was warmed under reflux for an additional 10 h, cooled to room temperature, and concentrated in vacuo. The residue was partitioned between 20 mL of acetonitrile and 20 mL of hexane. The acetonitrile layer was concentrated in vacuo to yield a brown oil which was chromatographed over 15 g of silica gel (ethyl acetate–hexane, 1:4) to afford 616 mg (95%) of cyano lactone 2: mp 76–77 °C; IR ($CH_2Cl_2$) 2250, 1765 cm$^{-1}$; NMR ($CDCl_3$, 90 MHz) $\delta$ 1.5 (s, 3 H, $CH_3$), 2.1 (m, 4 H, $CH_2$), 2.45 (m, 4 H, $=CCH_2$ and $CH_2CN$), 5.6–6.0 (m, 2 H, =CH).

Anal. Calcd for $C_{11}H_{13}NO_2$: C, 69.11; H, 6.81. Found: C, 68.70; H, 6.98.

***meso*- and *dl*-*rel*-(1*R*,5*S*,6*S*)-6-Methyl-10-oxo-11-oxatricyclo[4.3.2.0$^{1,5}$]undec-8-en-4-ylidenehydrazine [6 (*meso*) and 7 (*dl*)].** A solution of 1.0 g (3.15 mmol) of iodo nitrile 1 and 2.17 g (6.63 mmol) of hexamethyldistannane[9] in 60 mL of dry benzene was irradiated for 52 h under argon using a 450-W medium-pressure Hanovia lamp and Pyrex filter. The solution was concentrated and most of the tin residues were removed in vacuo (0.7 mm, room temperature for 30 min). The residual oil was subjected to MPLC (Lobar size B column; ethyl acetate–hexane, 1:4) to give 418 mg (42%) of starting iodo lactone 1, 94 mg (16%) of *meso*-azine 6, and 61 mg (10%) of *dl*-azine 7. Azine 6: mp 160–220 °C dec; IR ($CH_2Cl_2$) 1775, 1395, 1145 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 1.72 (s, 6 H, $CH_3$), 1.80 (ddd, $J$ = 13, 10.5, 8.5 Hz, 2 H), 2.30 (dddd, $J$ = 19.3, 10.9, 8.7, 2.2 Hz, 2 H), 2.48–2.56 (m, 6 H), 2.62 (ddd, $J$ = 19.3, 9.1, 1.0 Hz, 2 H), 2.70 (d, $J$ = 2.2 Hz, 2 H), 5.8 (dt, $J$ = 9.3, 2.1 Hz, 2 H, =CH), 6.06 (dt, $J$ = 9.3, 2.1 Hz, 2 H, =CH); $^{13}$C NMR ($CDCl_3$) $\delta$ 21.4 (q), 25.8 (t), 29.9 (t), 41.1 (t), 55.6 (s), 56.2 (d), 84.3 (s), 128.6 (d, two =CH), 166.6 (s), 177.1 (s); exact mass calcd for $C_{22}H_{24}N_2O_4$ *m/e* 380.1737, found *m/e* 380.1734.

Anal. Calcd for $C_{22}H_{24}N_2O_4$: C, 69.47; H, 6.32. Found: C, 68.92; H, 6.40.

Azine 7: mp 270–272 °C; IR ($CH_2Cl_2$) 1775, 1395, 1145 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 1.70 (s, 6 H, $CH_3$), 1.82 (ddd, $J$ = 13.0, 10.5, 8.5 Hz, 2 H), 2.18 (dddd, $J$ = 19.3, 10.7, 8.5, 2.3 Hz, 2 H), 2.48–2.56 (m, 6 H), 2.74 (d, $J$ = 2.3 Hz, 2 H), 2.82 (dd, $J$ = 19.3, 8.2 Hz, 2 H), 5.8 (dt, $J$ = 9.3, 3.2 Hz, 2 H, =CH), 6.06 (dt, $J$ = 9.3, 2.1 Hz, 2 H, =CH); $^{13}$C NMR ($CDCl_3$) $\delta$ 21.5 (q), 25.9 (t), 30.3 (t), 41.1 (t), 55.6 (s), 56.6 (d), 84.1 (s), 128.6 (d, two =CH), 166.9 (s), 176.8 (s); exact mass calcd for $C_{22}H_{24}N_2O_4$ *m/e* 380.1737, found *m/e* 380.1765.

***rel*-(1*S*,5*S*)-1-(3-Cyanopropyl)-5-methyl-6-oxabicyclo[3.2.1]oct-2-en-7-one (10) and *rel*-(1*S*,4*R*,5*R*,8*S*)-4-Cyano-8-methyl-9-oxatricyclo[6.2.1.0$^{1,5}$]undecan-10-one (12).** To a solution of 1.05 g (3.18 mmol) of iodo nitrile 8 in 50 mL of dry benzene under reflux was added a solution of 1.8 g (6.19 mmol) of tri-*n*-butyltin hydride and 20 mg of AIBN in 15 mL of dry benzene via syringe pump at a rate of 1.7 mL h$^{-1}$. The mixture was warmed under reflux for an additional 8 h, cooled to room temperature, and concentrated in vacuo. The residue was chromatographed over 40 g of silica gel (ethyl acetate–hexane, 1:4) to give 86 mg (13%) of tricyclic nitrile 12 and 463 mg (71%) of cyanolactone 10. Lactone 12: mp 78–80 °C; IR ($CH_2Cl_2$) 2240, 1775 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 1.5 (s, 3 H, $CH_3$), 1.8–2.2 (m, 8 H), 2.26 (dt, $J$ = 9, 9 Hz, 1 H, C*H*CHCN), 2.36 (m, 2 H), 3.13 (dt, $J$ = 9, 3.5 Hz, 1 H, CHCN); $^{13}$C NMR ($CDCl_3$) $\delta$ 20.99 (t), 25.7 (q), 29.69 (t), 30.52 (t), 32.04 (t), 35.43 (d), 40.24 (t), 42.98 (d), 51.06 (s), 83.92 (s), 120.22 (s), 179.87 (s); mass spectrum, *m/e* (relative intensity) 205 (27), 161 (100), 146 (92), 133 (51), 119 (47), 111 (57), 106 (75); exact mass calcd for $C_{12}H_{15}NO_2$ *m/e* 205.1103, found *m/e* 205.1136.

Anal. Calcd for $C_{12}H_{15}NO_2$: C, 70.24; H, 7.32. Found: C, 70.52; H, 7.63.

Lactone 10: IR ($CH_2Cl_2$) 2250, 1770 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 90 MHz) $\delta$ 1.52 (s, 3 H, $CH_3$), 1.8 (m, 6 H, $CH_2$), 2.4 (m, 4 H, $=CCH_2$ and $CH_2CN$), 5.6–5.9 (m, 2 H, =CH); $^{13}$C NMR ($CDCl_3$) $\delta$ 17.55 (t), 20.94 (t), 25.20 (q), 31.33 (t), 37.61 (t), 43.14 (t), 47.78 (s), 81.52 (s), 119.24 (s), 128.53 (d), 130.98 (d), 177.08 (s).

**Acknowledgment.** We thank the National Science Foundation for financial support. We thank Richard Weisenberger for recording mass spectra at the Ohio State University Campus Chemical Instrument Center.

**Registry No.** 1, 99310-22-2; 2, 99310-23-3; 6, 99310-24-4; 7, 99310-25-5; 8, 99310-26-6; 10, 99310-27-7; 12, 99310-28-8.

**Supplementary Material Available:** Crystallographic details and ORTEP drawings are available for compounds 7 and 12 (32 pages). Ordering information is given on any current masthead page.

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[12] Ogibin has reported the cyclization of several $\epsilon$-cyano radicals having $\alpha$-hydrogens to give cyclohexanones in low yield.[3] On the other hand, Johns has provided an example of an $\epsilon$-cyano radical cyclization which gives cyclohexanones in good yield.[4] In this case, the nitrile had no $\alpha$-hydrogens.

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# Preparation and Some Reactions of 1-(Trimethylsilyl)cyclopropanol and Its Trimethylsilyl Ether

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The chemistry of cyclopropylsilanes[1] has recently found synthetic applications in the area of cyclopentannulation through the thermal rearrangement of 1-(1-silylcyclopropyl)alkenes.[2] However, studies directed toward utilizing cyclopropylsilanes with electrophiles to afford ring-opened products are as of yet less promising, as the systems thus far explored at times exhibit carbocation rearrangements and variations in bond selectivity which limit generality.[3] In contrast, the facile ring-opening of

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