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THE SERENDIPITOUS SYNTHESIS OF AN OXABICYCLO[3.2.0]HEPTADIENE[†]

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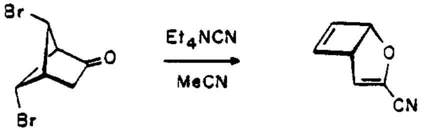
Abstract: 5,6-Dihalobicyclo[2.1.1]hexanes resist simple nucleophilic displacement in several ways. Least expected of these is the **2**→**1** rearrangement

The energy needed to assemble 2-oxabicyclo[3.2.0]heptadienes is normally supplied by photons.[1] An alternative source, the strain energy of a precursor, was once used to prepare the hexamethyl derivative, but only inefficiently (16%) and at a high temperature (190°)[2] We now report a novel rearrangement that enables precursor strain to provide the 3-cyano derivative (**1**)[3] at ambient temperature and in 65% yield



2 **1**

Evidence for the structural hypothesis (**1**) begins with the characteristic cyanovinyl ether infrared bands[4] at 2250(w), 1610(m), and 990(s) cm^{-1}. Bicyclic connectivity then follows from the two highest field ^1H and ^{13}C NMR signals (*f*, *g*, Table I). The further [3.2.0] partition is suggested by the cyclobutenoid $^1J_{CH}$ of *a* and *b*[5] and by the absence of any J_{HH} >3.5 Hz.[6a] The sole remaining alternative, a 4-cyano derivative, would have required $\delta_C(d) > \delta_C(c)$[6b] and $\delta_H(d)$ >6.5 ppm.[4b,6c] Proton assignments (Figure 1) are in accord with those of the parent heterocycle and its 1,3-dimethyl[1a] and 2,3-dihydro derivatives.[7]

Table I ^{13}C and ^1H NMR Spectra of **1** (1*M*, CD_3CN)

	δ_C[a]	$^1J_{CH}$[c]	δ_H[b]	A_H[d]	^1H NMR Appearance[c]	Notes
a	149.47	178	6.65	1.01	ddd, J = 2.8, 2.8, 0.2	[a]22.49 MHz.
b	136.94	176	6.01	1.01	dd, J = 2.7, 2.6	[b]80.00 MHz.
c	131.82	—	—	—	—	
d	122.66	165	6.18	1.02	d, J = 2.9	[c]Apparent coupling constants in Hz.
e	113.25	—	—	—	—	
f	84.19	167	5.32	1.00	dd, J = 3.5, 2.9	[d]^1H areas normalized to 5.
g	53.03	157	3.85	0.96	m	

[†] Dedicated to Professor W. von E Doering on the occasion of his sixty-fifth birthday

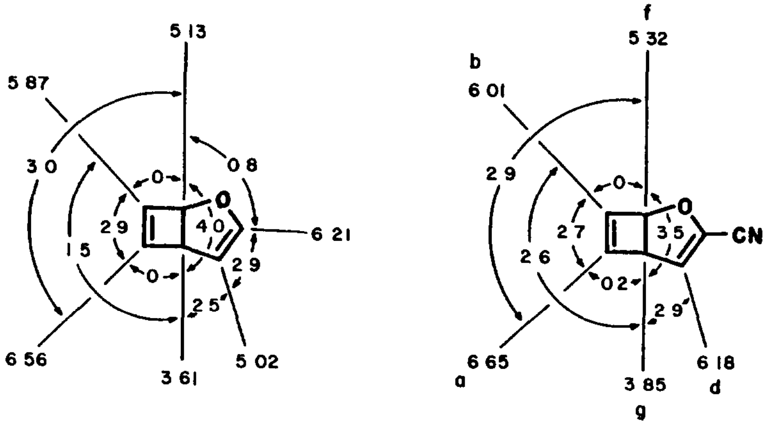
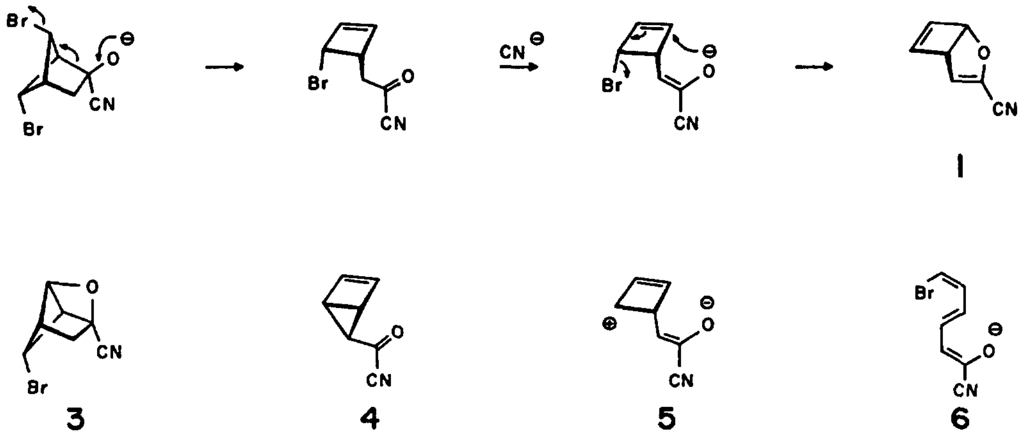


Figure 1. ^{1}H NMR chemical shift and apparent coupling constant assignments of 2-oxabicyclo-[3.2.0]heptadiene[1d] and **1**. All protons were sequentially decoupled.

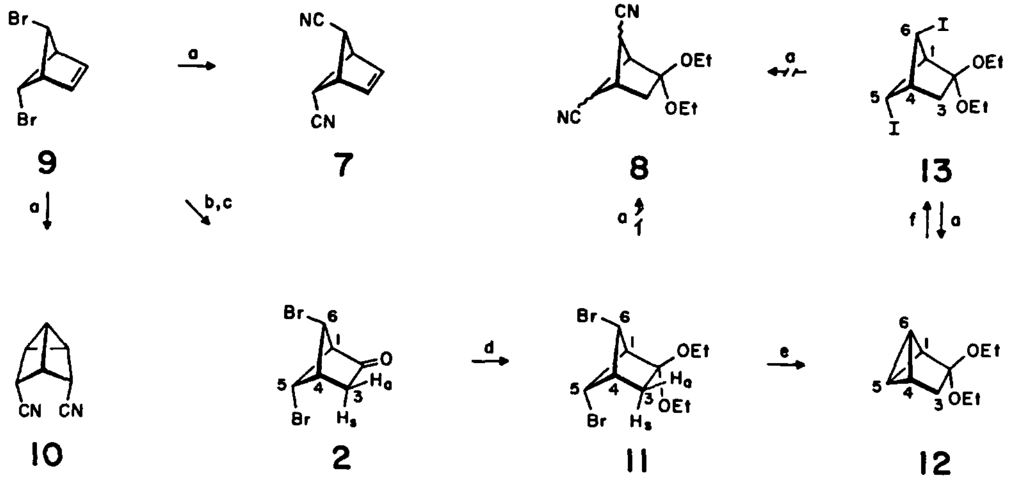
The corresponding mechanistic hypothesis (Scheme I) is less certain. As nucleophile to the carbonyl function of **2**, cyanide permits a stereoelectronically attractive heterolysis to exchange the angle strain of a cyclobutene for that of a bicyclo[2.1.1]hexane. As base, cyanide then allows the resulting enolate anion to execute a suprafacial S_N2' displacement.[8] However plausible the hypothesis, it ignores such potential intermediates as **3**-**6**. Scheme I thus serves to define a mechanistic problem, rather than to resolve it.

Scheme I



Our initial goal was neither structural nor mechanistic, but rather preparative: a 2-functionalized 5,6-dicyanobicyclo[2.1.1]hexane, *e.g.*, **7** or **8** (Scheme II). Benzvalene dibromide (**9**)[9a,b] provided **7**,[10] but only as byproduct of **10**[9b,c] and never in more than 6% yield. The cationic instability of **9**[9a,c] limited these efforts and suggested the dibromoketal (**11**,[11] 84% *via* **2**[12]) as a potentially more robust cyanide substrate. In practice, **11** was recovered unchanged by cyanide under various conditions, and so it was transformed to the diiodo diethyl ketal (**13**,[13] 64% *via* **12**[14]). This reacted efficiently, but only by a reductive dehalogenation[15] that regenerated its precursor (**12**). We thus turned back to the dibromoketone (**2**), and thereby discovered the remarkably facile rearrangement that provides 3-cyanooxabicyclo[3.2.0]heptadiene (**1**).

Scheme II



Reagents: a. Et$_4$NCN/MeCN, b. BH$_3$·THF, c. Na$_2$Cr$_2$O$_7$/H$_2$SO$_4$, d. HC(OEt)$_3$, e. *t*-BuLi, f I$_2$

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References and Notes

1. (a) Paquette, L.A.; Barrett, J.H. *J. Am. Chem. Soc.* **1966**, *88*, 1718; (b) Vogel, E., Günther, H. *Angew. Chem.* **1967**, *79*, 429; *Angew. Chem. Int. Ed. Engl.* **1967**, *6*, 385; (c) Holovka, J.; Gardner, P.D. *J. Am. Chem. Soc.* **1967** , *89*, 6390, (d) Holovka, J Ph.D. Thesis, University of Utah, 1969, *Diss. Abstr.* **1969** , *29*, 3260-B, (e) Rieker, A., Henes, G., Berger, S. *Chem. Ber.* **1975** , *108*, 3700; (f) Anastassiou, A.G., Reichmanis, E.; Girgenti, S.J., Schaefer-Ridder, M. *J. Org. Chem.* **1978** , *43*, 315.

2. Bauman, B.C ; Rey, M., Markert, J., Prinzbach, H., Dreiding, A.S. *Helv. Chim. Acta* **1971**, *54*, 1589.
3. **1**· *m/e* (70 eV)· 119 (67.0, p), 93 (100, p-C_2H_2). Calcd. (and obsd.) C 70.58 (70.35, 70.42), H 4.23 (4.17, 4.13), N 11.76 (11.95, 11.99).[16]
4. (a) Socrates, G. "Infrared Characteristic Group Frequencies", Wiley, Chichester, 1980, 33, 34, 39, 49; (b) Burrows, C.J., Carpenter, B.K. *J. Am. Chem. Soc.* **1981**, *103*, 6983.
5. Levy, G.C., Lichter, R.L., Nelson, G.L. "Carbon-13 Nuclear Magnetic Resonance Spectroscopy," 2nd Ed., Wiley, New York, 1980, 89.
6. Günther, H. "NMR Spectroscopy", Wiley, Chichester, 1980, (a) 110; (b) 373, (c) 99.
7. Paquette, L.A., Barrett, J.H., Spitz, R.P.; Pitcher, R. *J. Am. Chem. Soc.* **1965** , *87*, 3417.
8. Magid, R.M. *Tetrahedron* **1980**, *36*, 1901.
9. (a) Roth, R J.; Katz, T.J. *J. Am. Chem. Soc.* **1972** , *194*, 4770, (b) Roth, R.J. *Synth. Commun.* **1979**, *9*, 751, (c) Roth, R.J., Katz, T.J. *J. Org. Chem.* **1980**, *45*, 961.
10. **7**: mp 64° (hexane-ether); δ_H (C_3D_6O) 7.08 (2.03H, t, J = 2.1 Hz), 4.29 (1.05H, t, J = 2.4 Hz), 3.47(s) and 3.35(m) (2.93H), δ_C ($CDCl_3$) 140.28 (d, J = 185 Hz), 118.06(s), 117 32(s), 61.25 (d, J = 146 Hz), 58.96 (d, J = 162 Hz), 49.60 (d, J = 167 Hz).[16]
11. **11**· mp 44° (MeOAc), δ_H ($CDCl_3$) 5.10 (0.92H, q, J = 2.6 Hz, H5), 4.30 (0.95H, s, H6), 3.52 (3.91H, m, OCH_2), 3 06 (0.99H, dd, J = 7.8, 2.4 Hz, H1), 2.78 (0.97H, dm, J = 7.2 Hz, H4), 2.33 (1.02H, dd, J = 11 4, 1.5 Hz, $H3_s$), 1.96 (1.03H, ddd, J = 11.6, 1.8, 1.8 Hz, $H3_a$), 1.10 (6 21H, m, CH_3).[16]
12. **2**. mp 66° (isooctane), IR (KBr) 1755 cm^{-1}, δ_H ($CDCl_3$) 5.33 (0.93H, q, J = 3.0 Hz, H5), 4.30 (0.99H, s, H6), 3.35 (ddt, J = 7.0, 3.0, 1.5 Hz, H4) and 3.25 (1.97H, dd, J = 7 0, 3 0 Hz, H1), 2.90 (1.01H, dd, J = 17.0, 1.5 Hz, $H3_s$), 2 40 (1.09H, ddd, J = 17.0, 3.0, 1.5 Hz, $H3_a$). Calcd. (and obsd) C 28.38 (28.43), H 2.38 (2.46), Br 62.94 (62.82).[16]
13. **13** mp 86° (MeOH), δ_H ($CDCl_3$) 4.10 (1.9H, m, H5,6), 3.55 (3.8H, m, OCH_2), 3.17 (1.2H, dt, J = 7.1, 2.4 Hz, H1), 2.74 (1.2H, m, H4), 2 20 (2.0H, m, H3), 1.26 (6.8H, t, J = 7.5 Hz, CH_3), δ_C ($CDCl_3$) 104.85(s), 56.75 (t, J = 142 Hz), 55.78 (d, J = 162 Hz), 50.61 (*d*, J = 149 Hz), 36.75 (t, J = 139 Hz), 14 67 (q, J = 124 Hz), 11.46 (d, J = 165 Hz).[16]
14. **12** δ_H ($CDCl_3$) 3.23 (3 93H, m, OCH_2), 2 01 (dt, J = 5.1, 1.8 Hz, H1) and 1 90 (3.03H, m, H5,6), 1.73 (0.95H, m, H4), 1.23 (2.13H, q, J ≈ 0.9 Hz, H3), 0 90 (5.96H, t, CH_3); δ_C ($CDCl_3$) 113 15(s), 57.14 (t, J = 141 Hz), 38.25 (d, J = 170 Hz), 37.63 (t, J = 132 Hz), 30.78 (d, J = 167 Hz), 14.89 (q, J = 126 Hz), 5.05 (d, J = 215 Hz). Calcd. (and obsd.) C 71.39 (71 37), H 9 59 (9.68).[16]
15. Mazur, S.; Schroder, A H., Weiss, M C. *J. Chem. Soc. Chem. Commun.* **1977**, 262.
16. The reported yield is that of a product purified to these specifications

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