

for $K = \pm 3$, while much narrower widths (≤ 5 kHz) are predicted for $K = \pm 1$. For K states other than 0, ± 3 , and ± 6 to be forbidden, the symmetric top must have a 3-fold axis associated with three zero-spin nuclei.¹¹ These criteria are met by the molecular cluster $^{40}\text{Ar}_3\text{-H/DF}$, which is an oblate symmetric top.

Confirmation of this composition is provided by analysis of B_0 . Neglecting any tilt of the Ar_3 plane and vibrations other than torsional oscillations of the H/DF, we have¹³

$$I_{bb}(\text{cluster}) = (1/2)(1 + \cos^2\alpha)I_{bb}(\text{H/DF}) + I_{bb}(\text{Ar}_3) + \mu_c R^2 \quad (1)$$

where R is the distance between the H/DF and Ar_3 centers of mass (c.m.) and $I_{bb}(\text{Ar}_3)$ is a function of r , the Ar-Ar distance. For argon dimer, a B_0 of 0.05778 cm^{-1} has been determined from a high-resolution Raman study.¹⁴ It gives an r_0 of 3.821 \AA , which in eq 1 leads to values of 2.785 and 2.479 \AA for R in $\text{Ar}_3\text{-HF}$ and -DF . The smaller R for the DF species show that the H/D end is pointed at the Ar_3 . The corresponding H/DF c.m. to Ar distances of 3.553 and 3.525 \AA are comparable with the 3.510 and 3.461 \AA found in Ar-H/DF .² Also, the H/DF c.m. to Ar line is 38.5° from the c axis. A full account will be presented later, including the results of a search for the isotopic species $^{36}\text{Ar}_2\text{-H/DF}$ to determine accurate bond distances.

Registry No. Ar, 7440-37-1; HF, 7664-39-3; DF, 14333-26-7.

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Synthesis, Trapping, and Spectral Characterization of 1H-Cyclopropa[*l*]phenanthrene¹

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The cycloproparenes **1**,³ **2**,⁴ and **3**,⁵ and their derivatives are surprisingly stable, readily available materials.⁶ By comparison cyclopropa[*a*]naphthalene (**4**) explodes upon melting^{7a} and its 1,1-difluoro derivative^{7b} is stable in solution only at temperatures below -30°C . This decrease in stability perhaps reflects the formally enhanced olefinic character of the bridge bond. 1H-Cyclopropa[*l*]phenanthrene (**5**), the most important unknown structural variant within this family, should exemplify further this

(1) (a) Studies in the Cycloproparene Series. For the previous part, see ref 8; (b) Presented in part at the 7th I.U.P.A.C. Conference on Physical Organic Chemistry, Auckland, 1984; Abstract A28.

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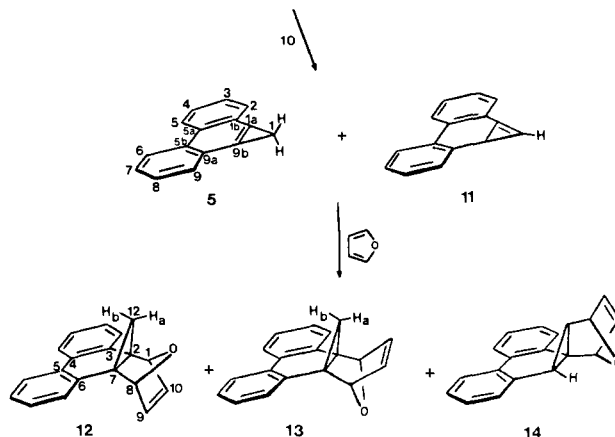
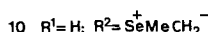
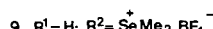
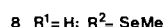
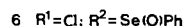
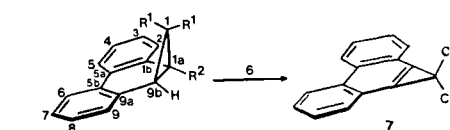
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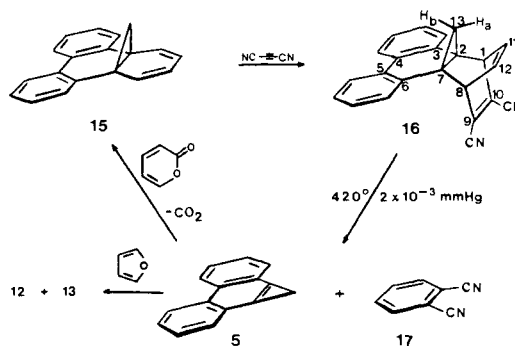
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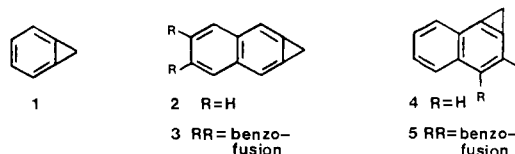
Scheme I



Scheme II



phenomenon. We now report syntheses of **5** and show it to be an unusually reactive molecule stable only at low temperatures.



Recent results have shown⁸ that *syn*-selenoxide elimination from **6** (Scheme I) occurs to give products derived from **7**. However, **7** could be neither isolated nor trapped because of facile cleavage of the three-membered ring. Despite its limitations, the study⁸ has provided the first definitive evidence for the existence of the 1H-cyclopropa[*l*]phenanthrene ring system and implies that an elimination across the 1a,9b-positions of an appropriate 1a,9b-dihydro derivative is the method of choice^{6,8,9} for the synthesis of **5**.

With this in view, selenide **8**^{10,11} has been transformed into the selenonium salt **9** which eliminates dimethyl selenide upon

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(10) Compound **8** is available from 9-bromophenanthrene in five steps: Dent, B. R.; Halton, B., manuscript in preparation.

(11) All new compounds reported provided satisfactory analytical and spectral data.

treatment with potassium *tert*-butoxide, probably¹² via the ylide **10**. The primary hydrocarbon products **5** and **11** cannot be isolated despite many variations in the reaction conditions. However, with added furan they are trapped as cycloadducts **12** (20%),^{13,14} **13** (13%),^{13,15} and **14** (7%)¹⁶ (Scheme I). The symmetry planes in **12** and **13** are evident from the appearance of only 10 resonances in their ¹³C NMR spectra^{14,15} and the orientation of the three-membered ring with respect to the oxygen bridge is confidently assigned from the deshielding influence the oxygen atom has upon the ¹H NMR shift of H12a in **12**. Thus **12** displays a one-proton doublet ($J = 4.6$ Hz) at 2.55 ppm for H12a, whereas the equivalent resonance in **13** (1.97 ppm, $J = 5.2$ Hz) is more shielded. It is interesting that the major isolable products emanate from **5**, formed by abstraction of the benzylic H9b of **10**. The appearance of **14**¹⁶ as a minor product reflects the loss of H1 from **10** to give **11**, which is known¹⁶ to add stereospecifically to furan to give **14**.

A complementary approach to **5**, free of competing elimination modes, employs retrodiene cleavage and parallels the successful syntheses of **13a** and **4**.^{7a} Thus vacuum pyrolysis of **16**,¹⁷ the dicyanoacetylene adduct^{7a} of **15**,¹⁸ followed by low-temperature manipulation of the product mixture, has provided a dibromodifluoromethane solution of **5**¹⁹ free of *o*-dicyanobenzene (**17**) (Scheme II). The NMR spectral data recorded at -60 °C are in full accord with **5**. The C1 methylene protons appear as a singlet (3.54 ppm) in the expected⁶ range for the cycloproparenes and the aromatic proton multiplets typify the phenanthrene system. The single high-field carbon resonance (23.6 ppm, C1) has the highest chemical shift (by 4 ppm) yet recorded for C1 of a C1-unsubstituted cycloproparene, but the magnitude of the C1-H coupling (170.9 Hz) is normal.⁶ Seven distinct aromatic carbon resonances are noted but the shielding of the ortho carbons C1b(9a) is reduced from the usual⁶ 14–16 ppm to ~6 ppm. Prepared in this way, **5** reacts with furan to give **12** (28%) and **13** (17%) and with α -pyrone to yield tetraene **15** (41%) (after loss of carbon dioxide below 0 °C) (Scheme II). On prolonged standing the solution of **5** decomposes even at -60 °C. However, **5** has been isolated as a moderately stable solid which decomposes slowly over a period of days at -78 °C.

Acknowledgment. Financial assistance from the New Zealand Universities Grants Committee (to B.R.D.) and an Alexander von Humboldt fellowship (to D.L.O.; 1984–1985) are acknowledged gratefully.

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(13) Compounds **12** and **13** may be named as *syn*- and *anti*-3,4:5,6-dibenzo-11-oxatetracyclo[6.2.1.1.2⁷.0^{2,7}]dodeca-3,5,9-triene, respectively.

(14) **12**: mp 179.5–180.5 °C. Anal. (C₁₉H₁₄O) C, H. ¹H NMR δ 0.58 (d, $J = 4.6$ Hz, H12b), 2.55 (d, $J = 4.6$ Hz, H12a), 5.26 (s, H1,8), 6.34 (s, H9,10), 7.20–7.30 (m, H14,15,18,19), 7.45–7.60 (m, H13,20), 7.85–7.95 (m, H16,17); ¹³C NMR δ 25.6 (t, C12), 35.6 (d, C2,7), 79.4 (d, C1,8) 123.6, 126.7, 127.9, 128.9 (all d, C13–20), 130.5 (s, C3,6), 134.5 (s, C4,5), 139.4 (d, C9,10).

(15) **13**: mp 183–185 °C. Anal. (C₁₉H₁₄O) C, H. ¹H NMR δ 0.77 (d, $J = 5.2$ Hz, H12b), 1.97 (d, $J = 5.2$ Hz, H12a), 5.36 (s, H1,8), 6.45 (s, H9,10), 7.25–7.35 (m, H14,15,18,19), 7.50–7.60 (m, H13,20), 7.95–8.05 (m, H16,17); ¹³C NMR δ 31.9 (s, C2,7), 35.2 (t, C12), 84.8 (d, C1,8), 123.5, 126.6, 128.0, 129.0 (all d, C13–20), 130.5 (s, C3,6), 133.1 (d, C9,10), 134.8 (s, C4,5).

(16) Compound **14** provides analytical and spectroscopic data in accord with those previously published: Coburn, T. T.; Jones, W. M. *J. Am. Chem. Soc.* **1974**, *96*, 5218–5227.

(17) Compound **16** may be named as 3,4:5,6-dibenzo-9,10-dicyano-tetracyclo[6.2.2.1.2⁷.0^{2,7}]trideca-3,5,9,11-tetraene: 67%, mp 214–215 °C. Anal. (C₂₃H₁₄N₂) C, H, N. ¹H NMR δ 0.32 (d, $J = 5.7$ Hz, H13b), 1.99 (d, $J = 5.7$ Hz, H13a), 4.80 (t, $J = 3.9$ Hz, H1,8), 6.38 (t, $J = 3.9$ Hz, H11,12), 7.30–7.45 (m, H15,16,19,20), 7.70–7.80 (m, H14,21), 7.90–8.00 (m, H17,18); ¹³C NMR δ 26.6 (t, C13), 32.6 (s, C2,7), 47.0 (d, C1,8), 114.1 (s, CN), 123.3, 127.5, 128.1, 129.0, 131.1 (all d, C11,12,14–21), 127.0, 133.4, 137.4 (all s, C3–6,9,10).

(18) Compound **15** is available from triphenylene in seven steps: Tokita, S.; Schopff, F.; Vogel, E. manuscript in preparation.

(19) 1*H*-Cyclopropa[*J*]phenanthrene (**5**): ¹H NMR δ 3.54 (s, H1), 7.68–7.80 (m, H3,4,7,8), 7.95–8.00 (m, H2,9), 8.75–8.85 (m, H5,6); ¹³C NMR δ 23.6 (t, $J_{CH} = 170.9$ Hz, C1), 124.1, 124.6 (both s, C1a,9b and C1b,9a), 125.3, 125.8, 127.4, 128.6 (all d, C2–9), 133.5 (s, C5a,5b).

Registry No. **5**, 278-91-1; **8**, 98420-55-4; **9**, 98420-57-6; **10**, 98420-58-7; **11**, 57741-39-6; **12**, 98420-59-8; **13**, 98523-81-0; **14**, 53137-63-6; **15**, 98420-60-1; **16**, 98420-61-2; **17**, 91-15-6; furan, 110-00-9; dicyanoacetylene, 1071-98-3; α -pyrone, 504-31-4.

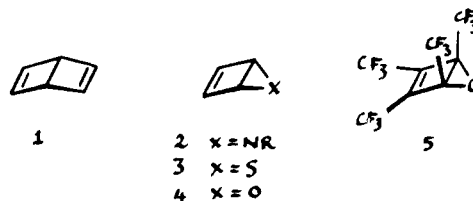
Dewar Furan: Its Generation and Trapping with Isobenzofuran

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It is now more than 20 years since van Tamelen and Pappas announced, in a landmark paper at that time, the preparation of the parent Dewar valence isomer **1** of benzene.² In contrast, the



heterocyclic Dewar valence isomers **2–4**³ remained unknown in unsubstituted form until 1985, when Strausz and his co-workers reported the trapping of Dewar thiophen (**3**), albeit in very low yield.⁴ Photoisomerization of the appropriate five-membered heterocycle has formed the major thrust for preparing such valence isomers and has been applied successfully to the generation of substituted Dewar thiophenes⁵ and Dewar pyrroles.⁶ However, irradiation of furans, while producing a variety of rearrangement products, offers no evidence for Dewar furans (5-oxabicyclo-[2.1.0]pent-2-enes).⁷ Indeed the few known examples,^{8,9} e.g., the perfluoromethyl derivative **5** reported by Lemal,⁸ have been prepared by indirect means.

Thus, in seeking a route to Dewar furan we designed the photochemical precursor **13** which is based on the established success of the 1,2-photoaromatization reaction to produce highly strained four-membered cyclic olefins.¹⁰ In this paper we discuss the results of this approach and announce the first example of the generation of Dewar furan **4** and its efficient trapping in adduct form with isobenzofuran (**15**).¹¹

The photosubstrate **13** was prepared as outlined in Scheme I.¹²

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