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TRANS-BICYCLO[7.4.0]TRIDECA-2,4,7,10,12-PENTAENE, 3,4-BENZOCYCLONONA-1,3,5,7-TETRAENE AND RELATED SUBSTANCES

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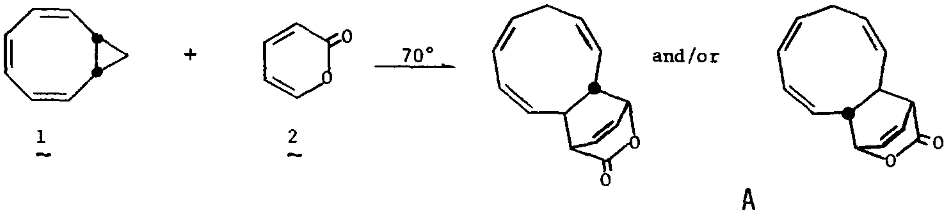
Recently we reported[2] that (4+2) cycloadditive trapping of thermally activated cis-bicyclo [6.1.0]nona-2,4,6-triene (1) yields a pair of trans-fused diastereomers incorporating monocyclic C_9 frames. Presently, we demonstrate the synthetic utility of this discovery with a description of several C_{13} carbobicycles, featuring the title compounds.[3]

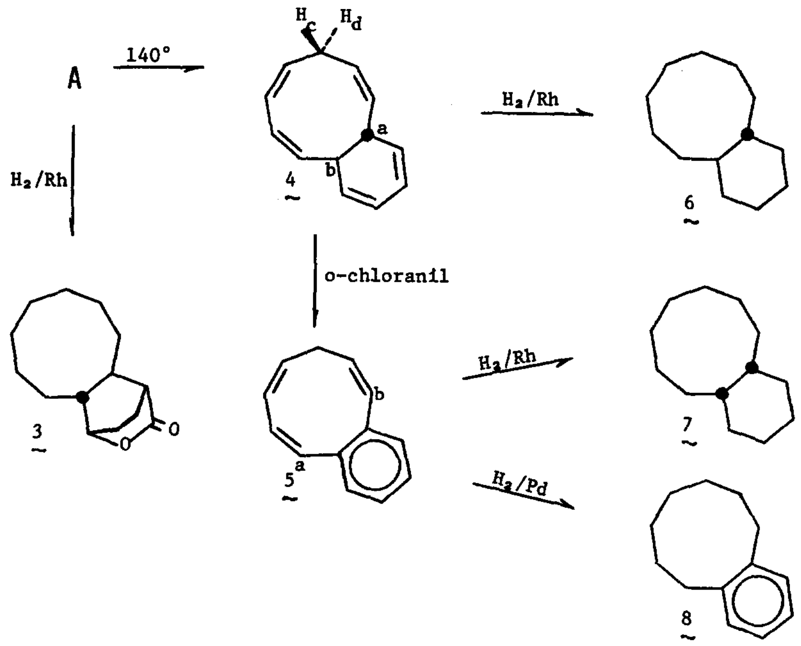
Prolonged (ca. 48 hr.) exposure of 1 to α-pyrone (2) at ca. 70°, produced what is believed to be a mixture of cycloadducts (mp 128°-142°) yielding a single pure component [mp 146-148°; ν_{CO}^{KBr} 1735 cm.$^{-1}$, $\lambda_{max}^{C_6H_{14}}$ 218 nm (sh) (ε 5040); nmr (100 MHz; $CDCl_3$) τ 3.46 (2H, t), 3.8-4.9 (7H, m), 6.60 (1H, m), 7.1-7.6 (3H, m), 7.92 (1H, dq); m/e 214 (P^+; 4.3%)] on successive fractional crystallization. Catalytic hydrogenation (Rh/C; 1 atm.) of the crude mixture of cycloadducts produced a perhydro derivative[4] 3 (or diastereomer thereof) [mp 81-82°; ν_{CO}^{KBr} 1730 cm.$^{-1}$, m/e 222] identical (mp, ir) with a synthetic sample prepared on reaction of trans-cyclononene[5] with 2 at 70°, followed by catalytic hydrogenation (Rh/C; 1 atm.) of the resulting cycloadduct. This information clearly requires that the cycloadducts of 1 and 2 incorporate monocyclic C_9 frames and, further, that these frames be fused trans to the remainder of the molecule. In addition, controlled degradation of specifically deuterated analogs established that the methylene group is, in each case, positioned γ to the trans bridge (vide infra). All available evidence thus points unequivocally to the structural assignment shown in A (or diastereomeric counterpart thereof)[6] for the cycloadduct(s) formed from 1 and 2.



1

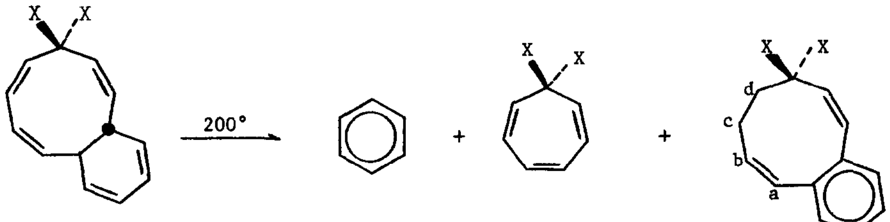
2

A



Careful vacuum thermolysis of A at 140° leads to a single $C_{13}H_{14}$ substance, 4 [colorless liquid; ν (neat) intense bands at: 2915, 915, 788, 780, 760, 720, 705 and 680 cm.$^{-1}$, $\lambda_{max}^{C_6H_{14}}$ 255 nm (sh) (ε 3300), 263.5 (3900), 273 (3800), 283 (sh) (2200); nmr (100 MHz; C_6D_6) τ 4.2-4.8 (10H, m), τ 6.8-7.3 (3H, m), τ 7.72 (1H, m, methylene proton); m/e 170 (P^+; 38%)]. The positional assignment of the methylene function of 4 derives from the nmr characteristics recorded under conditions of triple irradiation. Thus, when all coupling between "paraffinic" and "olefinic" protons was eliminated the "paraffinic" region was reduced simply to two *non-interacting* AB patterns with J_{ab} = 6.5 Hz and J_{cd} = 12.5 Hz. The stereochemical features of 4 follow from its catalytic hydrogenation (Rh/C; 1 atm.) to a $C_{13}H_{24}$ substance [m/e 180 (P^+; 24%)] 6, which differs (ir, gc) from *cis*-bicyclo [7.4.0] tridecane (7) obtained on catalytic hydrogenation (Rh/C; 1 atm.) of benzocyclononatetraene 5 (*vide infra*), and confirm ones expectation of stereochemical retention in the conversion of A to 4. Finally, the possession by this substance (4) of a [7.4.0] frame was unequivocally established by its conversion to benzocyclononatetraene 5 [colorless liquid; ν (neat) prominent maxima at: 2910, 1475, 1425, 770, 718 and 675 cm.$^{-1}$, $\lambda_{max}^{C_6H_{14}}$ 240 nm (sh) (ε 2950); nmr (60 MHz; $CDCl_3$) τ 2.80 (4H, s), 3.28 (1H, d, J = 10 Hz), 3.66 (1H, d, J=12.5 Hz), 3.9-4.9 (4H, m), 7.36 (2H, t, J = 6 Hz); m/e 168 (P^+; 100%)] on exposure to o-chloranil at 80°. The non-vicinal relationship between methylene and benzene shown in 5 follows unequivocally from the appearance in the nmr spectrum of *two* sharp one-proton doublets (H_a and H_b). This spectral feature is clearly inconsistent with the alternate isomeric arrangement, *i.e.*, 7,8-benzo CNT. As expected, 5 hydrogenates to the known[7] (ir, uv) tetrahydro derivative, benzocyclononene (8), when exposed to Pd/C catalyst and to the perhydro counterpart, 7 [m/e 180 (P^+; 28%)] when treated with Rh/C catalyst.

We now call attention to the location of the methylene group in 4 and 5 and the obvious implication of a similar structural feature in their cycloadduct progenitor (A) as well. The validity of this extrapolation was effectively confirmed with the use of 9,9-dideutero-*cis*-bicyclo [6.1.0]nona-2,4,6-triene (1-d_2), whereby A-d_2 [nmr (60 MHz; CDCl$_3$) τ 3.39 (2H, t), τ 3.7-5.0 (7H, m), 6.59 (1H, m), 7.25 (1H, m), 7.94 (1H, m)] containing a total of three "paraffinic" protons (nmr) was degraded to 5-d_2 [m/e 170 (P^+; 100%), nmr (60 MHz; CDCl$_3$) τ 2.79 (4H, *nm*), 3.27 (1H, d, J = 10 Hz), 3.66 (1H, d, J = 12.5 Hz), 3.9-4.7 (4H, m)] totally devoid of such hydrogens (nmr).



4 ; X = H
4-d_2 ; X = D

9 ; X = H
9-d_2 ; X = D

10 ; X = H
10-d_2 ; X = D

Finally, we find that brief exposure (10 min.) of 4 at 200° in benzene leads to its essentially quantitative (>90%) conversion into a mixture consisting (nmr) of *ca.* 35% benzene (nmr, ir), 35% tropilidine, 9 (nmr, ir, ms, uv) and 30% 10 [colorless liquid; ν (neat) prominent maxima at: 2920, 2855, 2790, 1430, 797, 770, 734, 712, 694 cm.$^{-1}$; $\lambda_{max}^{C_6H_{14}}$ 260 nm (sh) (ε 950); nmr (60 MHz; CDCl$_3$) τ 2.77 (4H, s), 3.65 (2H, d, H_a, J_{ab} = 11 Hz), 3.9-4.4 (2H, m, H_b) 7.8-8.2 (4H, m, H_c), 8.4-9.3 (2H, m, H_d); m/e 170 (P^+; 75%)].

The structure of 10 follows unambiguously from (i) the nmr spectrum with its obvious implication of molecular symmetry (presence of a two-proton doublet) and (ii) catalytic hydrogenation (Pd/C; 1 atm.) to benzocyclononene (ir, uv). With regards to operational detail, the use of specifically tagged 4, i.e., 4-d_2, established that both, isomerization of this substance to 10 and its fragmentation to 9 and benzene occur with full preservation of the integrity of the CH$_2$ group.

Specifically, 4-d_2 produced 9-d_2 (nmr)[8] and 10-d_2 (nmr) on brief (15 min.) thermolysis at 200°. Isomerization of 4 to 10 undoubtedly results from two consecutive 1,5 shifts involving H_a and H_b.[9]

We are actively investigating the chemistry of 4 and 5 with particular emphasis placed on the preparation of coveted monocyclic and ionic species.

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REFERENCES AND REMARKS

(1) National Science Foundation Graduate Trainee, 1969-present

(2) A. G. Anastassiou and R. C. Griffith, J. Amer. Chem. Soc., 93, 3083 (1971)

(3) The synthetic scheme realized here was first delineated in a research proposal submitted to the Petroleum Research Fund of the American Chemical Society on November 20, 1972.

(4) The crude hydrogenate had mp 78-82°. Two recrystallizations of this substance afforded pure 5 (or diastereomer thereof), with mp 81-82°.

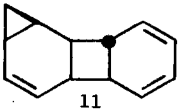
(5) A. C. Cope, D. C. McLean and N. A. Nelson, J. Amer. Chem. Soc., 77, 1628 (1955)

(6) For purposes of mechanistic interpretation, cycloadduct mixture A is currently being submitted to structural characterization.

(7) A. C. Cope and M. W. Fordice, J. Amer. Chem. Soc., 89, 6187 (1967)

(8) The referee expressed understandable concern about the lack of deuterium scrambling in 9-d_2 in view of the known thermal scrambling of the label of the 7-monodeutero analog under similar thermal conditions [A. P. Ter Borg, H. Kloosterziel and N. Van Meurs, Rec. Trav. Chim., 82, 717 (1963)]
We share the referee's surprise at what appears to be a rather substantial isotopic rate deceleration in the sigmatropic rearrangement of 9-d_2.

(9) We fully concur with the referee that the fragmentation of 4 into benzene and tropilidine is rationally interpretable through prior formation of an internal (2+4) cycloadduct, i.e., the trans-fused norcarene 11.



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