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A REVISED MECHANISM FOR THERMAL REARRANGEMENT OF SOME TRICYCLO[4.2.2.0^{2,5}]DECA-3,7,9-TRIENES

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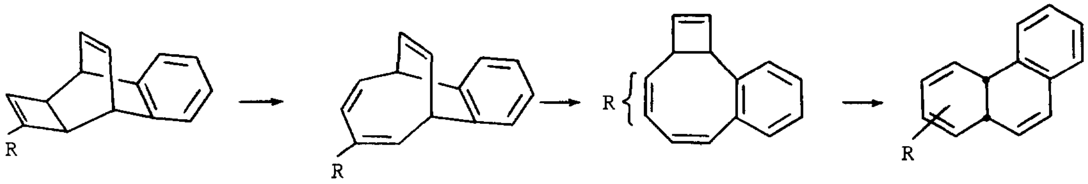
Nenitzescu's hydrocarbon (tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene) and several of its derivatives rearrange thermally to products having the bicyclo[4.4.0]decane skeleton[1]. It has been suggested that bicyclo[4.2.2]decatetraenes are reaction intermediates[1a,2], and a recent paper by Paquette and Stowell[3] presents evidence which is consistent with this proposal in the case of Ia and Ib (Fig. 1).

Fig. 1



Ia, R = H
Ib, R = CH_3

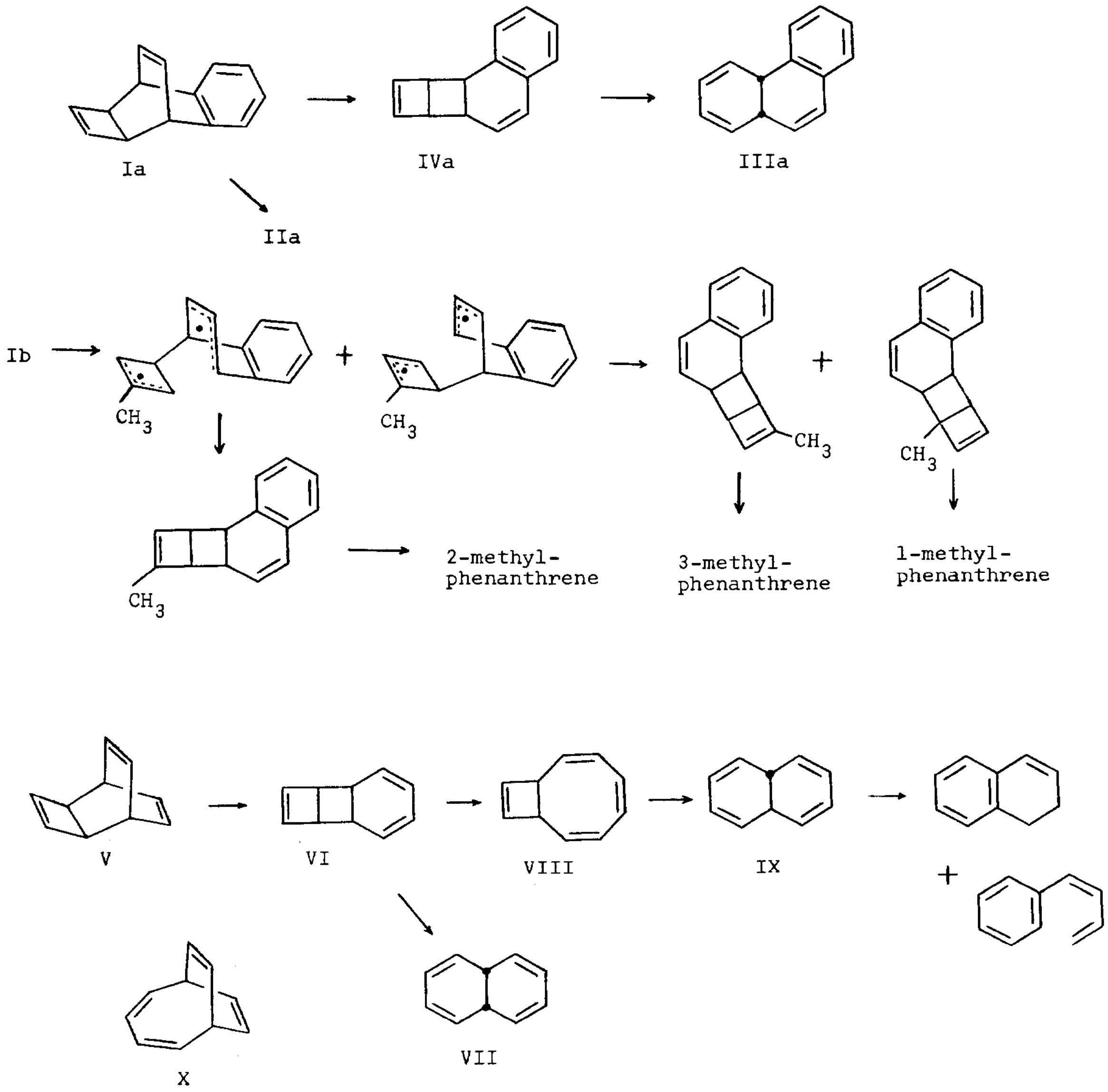
IIa,b

IIIa,b

We have also observed the thermal rearrangement of Ia[4], and while we agree that IIIa is the major product, our data require a different mechanism than that presented by Paquette and Stowell. Their postulated intermediate IIa can be isolated in addition to IIIa from flow pyrolyses conducted at 280°. Under these conditions, IIa is completely stable, and does not rearrange to IIIa below 350° using similar contact times. Thus, Ia must rearrange to IIIa by a mechanism which does not involve IIa as a significant intermediate at 280°.

We favor an alternate mechanism (Fig. 2) which explains the thermal rearrangement of Ia as well as rearrangements of other known tricyclo[4.2.2.0^{2,5}]-decatrienes.[1,2,3] The first step, conversion of Ia to IVa, may be regarded as a Cope rearrangement or a diradical process.[5] At present, we are unable to distinguish between these possibilities in the case of Ia, but the diradical pathway accounts correctly for the interesting distribution of methylphenanthrenes from pyrolysis of Ib[3]. The final step, opening of IVa to IIIa, explains the appearance of cis-fused IIIa to the exclusion of trans-fused product which might be expected from a benzo[10]annulene intermediate.[2,3]

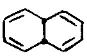
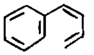
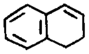
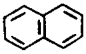
Fig. 2



Our mechanism can be applied to the parent hydrocarbon V with interesting results. The first step, interconversion of V and VI, has already received some publicity[6], and the sequence V → VI → VII should be analogous to the process I → IV → III in the benzo series. However, VI has available a new alternative which is blocked by benzo-annelation in the case of IVa, namely symmetry-allowed opening to VIII. A sequence of symmetry-allowed steps[7] may then convert VIII to the products 1,2-dihydronaphthalene and cis-1-phenylbutadiene.

We have reexamined the flow pyrolysis of V[1b] and X[8] under our usual conditions (280°). The results (Table 1) show conclusively that at least 90% of the products from V do not arise via X as suggested by others[1a,2]. We have also found that cis-1-phenylbutadiene is formed upon pyrolysis of trans-9,10-dihydronaphthalene IX, in addition to 1,2-dihydronaphthalene and naphthalene[9]. Thus, circumstantial evidence supports a closely related mechanism for rearrangement of both Ia and V. In both cases, opening to a bicyclo[4.2.2]decatetraene intermediate plays no major role in the rearrangements. Syntheses of IV and VI are in progress, and will be discussed along with appropriate kinetic studies in a full paper.[10]

Table 1 (Flow pyrolysis, 280°)

Starting Material	Products (GLPC, 10' Carbowax/chromosorb P)			
Ia	IIa (13%)	IIIa (85%)	Aromatized dihydrophenanthrenes (2%)	
V	 (7%)	 (8%)	 (84%)	 (1%)
X	" 86%	" trace	" 2%	" 6%

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9) *cis*-1-Phenylbutadiene has been isolated from pyrolysis of the sodium salt of bicyclo[6.1.0]-9-carboxaldehyde tosylhydrazone, a reaction which also produces *trans*-9,10-dihydronaphthalene IX (apparently via VIII) and 1,2-dihydronaphthalene[7c].

10) The mechanism for rearrangement of IIa to IIIa remains in doubt. At 370°, Ia is 98% converted to IIIa (72%), IIa (11%), phenanthrene (5%), aromatized dihydrophenanthrenes (7%), and naphthalene (1%).

Under identical conditions, IIa is converted to the extent of only 15% to IIIa (86%), phenanthrene (4%), aromatized dihydrophenanthrenes (6%), naphthalene (1%), and unknown products (3%). The similarity in product distribution implies a common mechanism for both reactions; the unprecedented conversion IIa → Ia provides an intriguing, but tentative explanation.

11) Vapors of the various hydrocarbons were swept through a heated pyrex column packed with pyrex beads, using purified nitrogen at atmospheric pressure as carrier gas. The products were trapped at -70° and analyzed directly by glpc. A two-fold increase in pyrolysis column surface area at constant contact time did not affect product ratios.