

## Low-temperature Photolysis of Some C<sub>9</sub>H<sub>10</sub> Hydrocarbons. A New Cyclononatetraene

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**Summary** Direct evidence is presented that (*cis*)<sup>4</sup>-cyclonona-1,3,5,7-tetraene and the new (*cis*)<sup>3</sup>,*trans*-cyclonona-1,3,5,7-tetraene are formed in the photolysis of some C<sub>9</sub>H<sub>10</sub> hydrocarbons.

RECENT reports<sup>1</sup> on photochemical rearrangements of some C<sub>9</sub>H<sub>10</sub> hydrocarbons suggest the involvement of thermal reactions of some labile unknown isomers. We present evidence to demonstrate that (*cis*)<sup>4</sup>-cyclononatetraene<sup>2</sup> and the new (*cis*)<sup>3</sup>,*trans*-cyclononatetraene are indeed formed in the photolysis of these compounds, using low-temperature techniques.<sup>3</sup> Compounds used were *cis*-bicyclo[6,1,0]nona-2,4,6-triene (1),<sup>2,4</sup> *trans*-bicyclo[6,1,0]nona-2,4,6-triene (2),<sup>1a</sup> *cis*-8,9-dihydroindene (3), *trans*-8,9-dihydroindene (4), (*cis*)<sup>4</sup>-cyclononatetraene (5).<sup>2</sup>

An analysis was performed by g.l.c. on the perhydro-derivatives, using both a UCW 98 and a Reoplex column to effect complete separation of the components. Compounds (1)–(6) (*vide infra*) were separately hydrogenated under the same conditions to provide the corresponding perhydro-compounds (1), 96% yield; (2), 96; (3), 93; (4), 94; (5), 99; (6), 94. Thus the reliability of this method was confirmed.† (iii) A portion was heated to 50° for 1 hr. and then hydrogenated in the same manner as described in method (ii). Therefore, methods (i) and (iii) should provide a very similar product distribution.

The Table summarizes the results of photolysis of (1)–(3) and (5) and shows that these compounds provide five compounds in somewhat similar proportions. Compound (6) is the only one to which no structure has been assigned.

TABLE  
Product distribution (%)

Analytical method: Product	Starting material											
	(1) <sup>a</sup>			(2) <sup>b</sup>			(3) <sup>c</sup>			(5) <sup>d</sup>		
	(i)	(ii)	(iii)	(i)	(ii)	(iii)	(i)	(ii)	(iii)	(i)	(ii)	(iii)
(1)	9	9	9	5	5	5	12	11	9	6	5	5
(2)	36	36	35	43	39	37	23	22	18	18	14	16
(3)	9	6	10	10	4	10	20	11	17	12	7	13
(4)	31	2	27	24	2	24	20	4	19	15	2	13
(6)	3	2	6	6	8	7	5	2	8	7	4	4
(A) + (B)	—	28	—	—	21	—	—	19	—	—	20	—

*cis*-Decalin used throughout as standard.

Methods (ii) and (iii) show the product distribution of the perhydro-compounds: see text.

Length of photolysis (minutes): <sup>a</sup> 150; <sup>b</sup> 40; <sup>c</sup> 330; <sup>d</sup> 165.

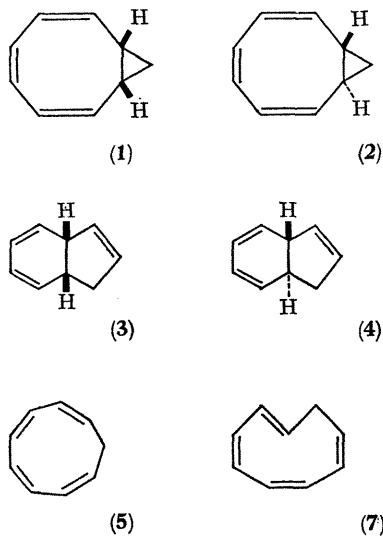
After the photolysis of (1) in tetrahydrofuran (0.8 M) at –60° with a low-pressure lamp (2537 Å)<sup>3</sup> reached a photo-stationary state (150 min.) the photo-product was analysed. (i) A portion was injected directly into a gas chromatograph (F and M 5750, UCW 98, column temp., 90°). In this process, thermally labile material underwent immediate rearrangement at the injection port. (ii) A portion was kept at –70° and hydrogenated with rhodium catalyst.<sup>3a</sup>

Compound (4) behaved photochemically quite differently from (1)–(3) and (5), and was isomerized slowly only to (6). Most important are the findings that cyclononane precursors [28% in the case of (1), method (ii)] were present in the cold photolysate, and that upon warming the amount of (3) (from 6 to 10%) and (4) (from 2 to 27%) increased at the expense of the precursors. These results indicated that a cyclononatetraene or a mixture of its geometrical

† All the perhydro-compounds were identical with those prepared according to literature procedures.<sup>5</sup> We thank Professor E. J. Corey and Dr. J. I. Shulman for providing us with spectra of perhydro-(2).

isomers was involved in the photolysis and we further investigated the thermal behaviour of these compounds.

After (1) was photolysed as described above, the photolysate was kept at  $-15^\circ$  and portions were withdrawn at intervals and hydrogenated at  $-70^\circ$  with rhodium catalyst. Finally, the sample was warmed to  $50^\circ$  and treated as above. The product distribution of perhydro-compounds clearly demonstrates that a cyclononatetraene (B) was converted at  $-15^\circ$  into (4) (first order kinetics) and that



the other (A) was rather stable and isomerized only after heating at  $50^\circ$ , to provide (3). That (A) is indeed (5) was proved in the following way. Treatment of cyclononatetraene<sup>2</sup> with methanol at  $-70^\circ$  followed by fractional distillation at  $-10^\circ/0.4$  mm. Hg, provided pure (5) which underwent thermolysis to afford (3) quantitatively as evidenced by the n.m.r. spectrum and g.l.c. This rearrangement was followed by u.v. spectra:  $k$  (at  $35.1^\circ$ ) =  $(6.55 \pm 0.13) \times 10^{-4}$ ,  $k$  (at  $15.0^\circ$ ) =  $(5.38 \pm 0.11) \times 10^{-5}$ ,  $\Delta H^\ddagger = 21.4 \pm 0.04$  kcal./mol, and  $\Delta S^\ddagger = -3.9 \pm 1.2$  e.u.<sup>†</sup> These results are consistent with the assignment of structure (5) to compound (A) and further suggest that (B) is a geometrical isomer of (5), very likely (*cis*)<sup>3</sup>, *trans*-cyclonona-1,3,5,7-tetraene (7), which is predicted to provide (4).

The observation that the photolysis of (1)—(3), and (5) provide a similar product distribution except for the starting material in each case strongly suggests that all these compounds and (7) constitute a photochemical *pool* (stationary state) and that slow leakage occurs upon prolonged irradiation to produce (6) from (4) and other polymeric material. The photochemical behaviour of the  $C_9H_{10}$  hydrocarbons is very similar to that observed for  $[CH]_{10}$  hydrocarbons and the thermal stability of (5) and (7) is comparable to that of (*cis*)<sup>5</sup>- and (*cis*)<sup>4</sup>, *trans*-[10]-annulenes, although the latter compounds are less stable. It is highly probable that interconversion of (5) and (7) is an important process of low-temperature photolysis.<sup>§</sup>

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<sup>†</sup> Kinetic measurements were performed by Dr. R. T. Seidner of this laboratory.

<sup>§</sup> After submission of this manuscript, we succeeded in isolating (7) (nearly pure) which underwent isomerization to (4) (n.m.r. and g.l.c.) at a rate very similar to that described above.

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