Low-temperature Photolysis of Some C_9H_{10} Hydrocarbons. A New Cyclononatetraene

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Summary Direct evidence is presented that $(cis)^4$-cyclonona-1,3,5,7-tetraene and the new $(cis)^3$,*trans*-cyclonona-1,3,5,7-tetraene are formed in the photolysis of some C_9H_{10} hydrocarbons.

RECENT reports[1] on photochemical rearrangements of some C_9H_{10} hydrocarbons suggest the involvement of thermal reactions of some labile unknown isomers. We present evidence to demonstrate that $(cis)^4$-cyclononatetraene[2] and the new $(cis)^3$,*trans*-cyclononatetraene are indeed formed in the photolysis of these compounds, using low-temperature techniques.[3] Compounds used were *cis*-bicyclo[6,1,0]-nona-2,4,6-triene (**1**),[2,4] *trans*-bicyclo[6,1,0]nona-2,4,6-triene (**2**),[1a] *cis*-8,9-dihydroindene (**3**), *trans*-8,9-dihydroindene (**4**), $(cis)^4$-cyclononatetraene (**5**).[2]

After the photolysis of (**1**) in tetrahydrofuran (0·8 M) at −60° with a low-pressure lamp (2537 Å)[3] reached a photostationary 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.[3a] 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**)[a] (i)	(ii)	(iii)	(**2**)[b] (i)	(ii)	(iii)	(**3**)[c] (i)	(ii)	(iii)	(**5**)[d] (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): [a] 150; [b] 40; [c] 330; [d] 165.

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

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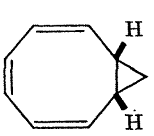
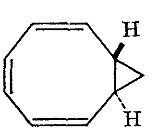
† All the perhydro-compounds were identical with those prepared according to literature procedures.[5] We thank Professor E. J. Corey and Dr. J. I. Shulman for providing us with spectra of perhydro-(**2**).

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° and portions were withdrawn at intervals and hydrogenated at −70° with rhodium catalyst. Finally, the sample was warmed to 50° and treated as above. The product distribution of perhydro-compounds clearly demonstrates that a cyclononatetraene (**B**) was converted at −15° into (**4**) (first order kinetics) and that the other (**A**) was rather stable and isomerized only after heating at 50°, to provide (**3**). That (**A**) is indeed (**5**) was proved in the following way. Treatment of cyclononatetraenide[2] with methanol at −70° followed by fractional distillation at −10°/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°) = $(6·55 \pm 0·13) \times 10^{-4}$, k (at 15·0°) = $(5·38 \pm 0·11) \times 10^{-5}$, $\Delta H^{\ddagger} = 21·4 \pm 0·04$ kcal./mol, and $\Delta S^{\ddagger} = -3·9 \pm 1·2$ e.u.[‡] 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*)[3], *trans*-cyclonona-1,3,5,7-tetraene (**7**), which is predicted to provide (**4**).


(**1**)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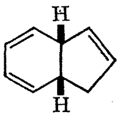
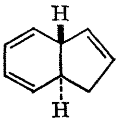
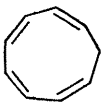

(**3**)


(**4**)


(**5**)


(**7**)

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*)[5]- and (*cis*)[4],*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.[§]

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[‡] Kinetic measurements were performed by Dr. R. T. Seidner of this laboratory.

[§] 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.

[1] (a) E. Vogel, W. Grimme, and E. Dinné, *Tetrahehron Letters*, 1965, 391; (b) G. J. Fonken and W. Moran, *Chem. and Ind.*, 1963, **1841**.

[2] T. J. Katz and P. J. Garratt, *J. Amer. Chem. Soc.*, 1964, **86**, 5194; E. A. LaLancette and R. E. Benson, *ibid.*, 1965, **87**, 1941.

[3] (a) S. Masamune and R. T. Seider, *Chem. Comm.*, 1969, 542; (b) S. Masamune, R. T. Seider, H. Zenda, M. Wiesel, N. Nakatsuka, and G. Bigam, *J. Amer. Chem. Soc.*, 1968, **90**, 5286.

[4] E. Vogel, *Angew. Chem.*, 1961, **73**, 548; E. Vogel, W. Wiedemann, H. Kieser, and W. F. Harrison, *Tetrahedron Letters*, 1963, **673**.

[5] E. LeGoff, *J. Org. Chem.*, 1964, **29**, 2048; A. C. Cope and J. K. Hecht, *J. Amer. Chem. Soc.*, 1963, **85**, 1780; N. L. Allinger and J. L. Coke *ibid.*, 1960, **82**, 2553.