[10]Annulenes

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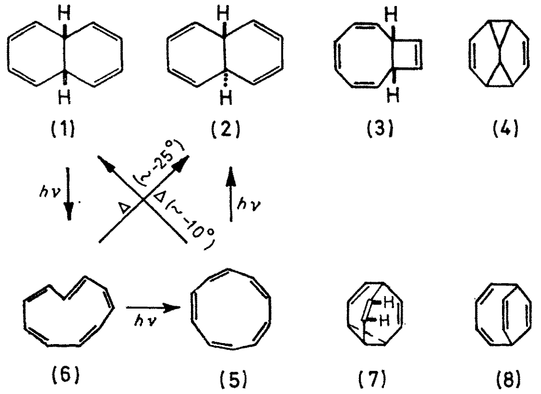
RECENTLY van Tamelen and Burkoth[1] claimed that (i) *cis*-9,10-dihydronaphthalene (**1**) showed no promise as an annulene (cyclodecapentaene) precursor; (ii) irradiation of the *trans*-isomer (**2**) by unfiltered light (2537 Å) from a Rayonet photochemical reactor *at* −190° *for* 2 *min.*[1] provided a cyclodecane precursor (or precursors); and (iii) *di-imide* reduction of the photolysate afforded cyclodecane *in as high as* 40% *overall yield.* The result of our extensive studies on the same subject is now found to be in conflict with theirs at least in these three respects. Use of the low-temperature techniques recently developed[2] has permitted us to observe for the first time what we believe to be n.m.r. signals of [10]annulenes and thus to define photolytic conditions under which these compounds are formed. Our findings are: (i) Only the *cis*-compound (**1**), not (**2**) or bicyclo[6,2,0]deca-2,4,6,9-tetraene (**3**), provided [10]annulenes in moderate yields under carefully controlled conditions. (ii) Photochemical reactions of (**1**), (**2**), and (**3**) are temperature-dependent and proceeded very fast at 0°, whereas these compounds were recovered unchanged after 7 hr. irradiation at −190°. (iii) As noted earlier,[2] di-imide is not a particularly effective reducing agent at low temperatures and the reduction was found not to compete favourably with thermolyses of [10]annulenes. Furthermore, we have now found the conditions under which hydrogenation proceeds efficiently at temperatures as low as −70°.



The Table summarizes the results of the photochemical experiments performed over a wide range of temperature under the conditions described previously;[2,3] the reaction was followed mainly by means of n.m.r. spectroscopy. Because of the thermal instability of tetracyclo[4,4,0,0^{2,10},0^{5,7}]deca-3,8-diene (**4**),[2] and [10]annulene-I (**5**) and -II (**6**) (*vide infra*) the product distribution of the photolyses performed above −40° was different from that at lower temperatures. The solvent systems employed were viscous around −100 to −130° and formed transparent glasses at

				Product distribution after *x* min. irradiation[b]						
Entry	Starting material[a]	Irrad. temp.	First half-life (min.)	**(4)**	**(1)**	**(2)**	**(7)**	**(5)**	**(6)**	*x*
I	**(1)**	−190	—	0	100	0	0	0	0	420
II	**(1)**	−110	35	65	8	19	7	tr.	0	240
III	**(1)**	−60	12	40	15	0	23	7	15	80
IV	**(1)**	0	7	[40% of **(8)**]	18	15	25	0	0	80
V	**(3)**	−190	—	0	0	0	0	0	0	420
VI	**(3)**	−110	40	63	11	13	10	tr.	0	180
VII	**(3)**	−60	16	60	10	17	6	1—2	0	85
VIII	**(2)**	−190	—	0	0	100	0	0	0	480
IX	**(2)**	−110	90	55	10	30	5	tr.	0	120
X	**(2)**	−60	55	55	14	22	7	1—2	0	180

[a] 0·35—0·45 M, in [$^2H_8$]tetrahydrofuran for −60° and −110° irradiation or in 1 : 1 [$^2H_8$]tetrahydrofuran–[$^2H_6$]ethanol for −190° and −110° irradiation with a low-pressure mercury lamp.

[b] By n.m.r. integration, and verified by g.l.c. [in consideration of reactions **(4)** → **(8)**, **(5)** → **(1)**, and **(6)** → **(2)**].

−190°. Presumably most significant was the finding of new signals† [a temperature-dependent signal (A) centred at τ 4·16 (−40°), and a sharp, temperature-independent, singlet (B) at τ 4·34] and these signals were moderately intense *only in the photolysis of* **(1)** *performed between* −50° *and* −70°. Compounds **(2)** and **(3)** provided only minor quantities (if any) of compounds responsible for these signals at any temperatures with the photo-apparatus we used.

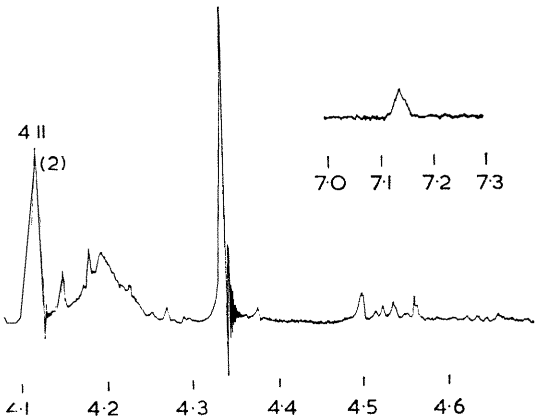


FIGURE 1

That the new signals were due to **(6)** and **(5)** was strongly supported by the experiments described below. When a 1·0M-solution of **(1)** in deuteriomethylpentane was irradiated at −60° and then cooled at −110°, there were formed crystalline precipitates consisting of a mixture of **(4)** and bullvalene **(7)**. The n.m.r. spectrum of the filtrate‡ taken at −40° is shown in Figure 1. Between −80° and −40° signal (A) was temperature-dependent (broadened at lower temperatures, *reproducible*) and all the others were temperature-independent. After standing at −25° for 2 hr., most of signal (A) disappeared and the formation of **(2)** was apparent (τ 4·11, 8H, 7·14, 2H)[2] (Figure 2). Further warming the sample at −10° for 2 hr. increased the intensity of the signals of **(1)** (multiplet around τ 4·6 and 4·2, 8H, 6·75, 2H) at the expense of (B) and at similar rate **(4)** isomerized to bicyclo[4,2,2]deca-2,4,7,9-tetraene **(8)**[2] Figure 3). From these spectral data, we conclude that all the thermal rearrangements of **(4)**, **(5)**, and **(6)** are essen*tially* quenched below −50°. The final product identification and distribution were further confirmed by g.l.c.

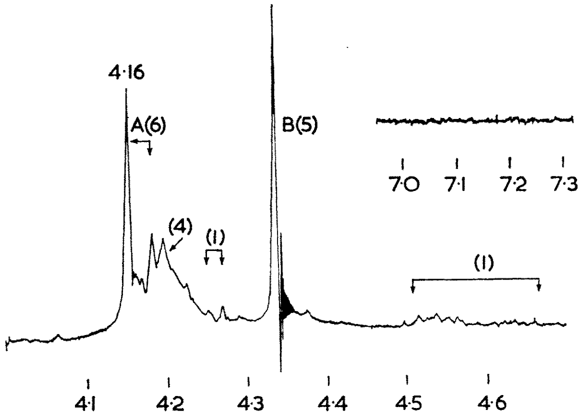


FIGURE 2

Hydrogenation of the compounds responsible for signals (A) and (B) was achieved by bubbling hydrogen through a cold (−70°) ethanolic solution of the filtrate described above with rhodium catalyst.[4] The product, obtained in more than 80% yield based on the calculated amount of (A) and (B), was identical in every respect (i.r., n.m.r.,

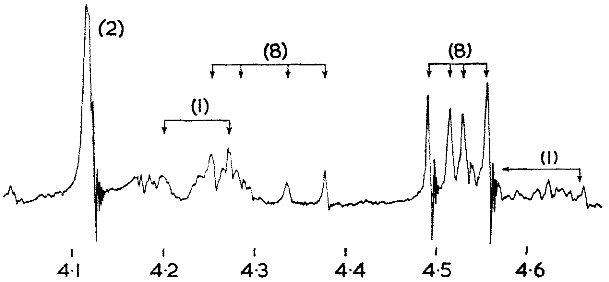


FIGURE 3

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† Hitherto eleven $[CH]_{10}$ hydrocarbons have been known and characterized by their n.m.r. spectra.[2]

‡ The filtration was carried out below −60°. In the region between τ 0—12 only observable signals were A, B and those of **(4)**, **(1)**, and a trace of **(7)**. Chemical shifts of some compounds were slightly temperature-dependent.

mass spec., g.l.c.) with cyclodecane. Control experiments demonstrated that none of the other compounds [(**1**), (**2**), (**4**), and (**7**)] present in the photolysate gave cyclodecane under similar conditions.

The above result permits the assignment of [10]annulene structures to the compounds exhibiting signals (A) and (B). Furthermore, the assignment of all-*cis*-geometry to (B) (see **5**) is consistent with (i) observation of a sharp singlet, indicating conformational changes are occurring rapidly; and (ii) formation of (**1**) on warming, providing that the selection rule is applicable to this system. Similarly, one *trans*-double bond may be assigned to (A) (see **6**). Thus for the first time evidence is presented to show that [10]annulenes exhibit no significant diamagnetic circulation around the ring system, and are thermally isomerized stereospecifically (at least, within the limits of the sensitivity of the spectrometer) to 9,10-dihydronaphthalenes.

Obviously the photolysis of any single starting material is extremely complex (see the Table) because it involves concurrent photoisomerizations of other compounds including (**5**) and (**6**) and detailed discussions should be deferred until adequate experimental support is obtained. However, two comments are offered, using (**1**) as an example. (i) Photo-induced ring opening of (**1**) competes with an efficient process leading to (**4**). If the assumption is correct that this opening is stereospecific

$$[\text{conrotatory, } (\mathbf{1}) \xrightleftharpoons{h\nu} (\mathbf{6}), \text{ accordingly } (\mathbf{2}) \xrightleftharpoons{h\nu} (\mathbf{5})],$$

then the formation of (**2**) from (**1**) indicates that (**1**) is transformed into (**6**) first, and that (**6**) isomerizes to (**5**) *photochemically* because no thermolyses of these compounds are occurring below −50° (*vide supra*). (ii) The process leading from the excited state of (**1**) to that of (**6**) is not (nearly) isoenergetic, but in view of the expected large instability (particularly ring strain) of the latter system, there intervenes a relatively large energy barrier. Thus this process is temperature-dependent [*cf.*, half lives of (**1**), (**2**), and (**3**) at various temperatures] and is extremely slow at −190°. In contrast, any photoisomerization processes of (**6**) [(**6**) to (**5**), (**6**) to (**1**)] is relatively temperature-independent. Therefore, it is conceivable that at higher temperature (−60°) formation of (**6**) favourably competes with the disappearance of (**6**), which accumulates in the photo-mixture.

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[1] E. E. van Tamelen and T. L. Burkoth, *J. Amer. Chem. Soc.*, **1967**, **89**, **151**. A detailed description of their photolysis and reduction was kindly supplied by the authors. Unfortunately, we have not been able to reproduce their results. However, our failure could possibly be due to the subtle differences in experimental conditions.

[2] S. Masamune, R. T. Seidner, H. Zenda, M. Wiesel, N. Nakatsuka, and G. Bigam, *J. Amer. Chem. Soc.*, 1968, **90**, 5286. Leading references for the chemistry of $[CH]_{10}$ hydrocarbons are quoted therein. Regarding properties of (**2**) and the di-imide reduction, see footnotes 2 and 11, respectively.

[3] S. Masamune, R. T. Seidner, and H. Zenda, submitted to *J. Org. Chem.* A detailed description of the photo-apparatus is given.

[4] H. C. Brown and C. A. Brown, *J. Amer. Chem. Soc.*, 1962, **84**, 1494. Of at least ten catalysts tested, only rhodium was effective.