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[12]ANNULENE 1)

by

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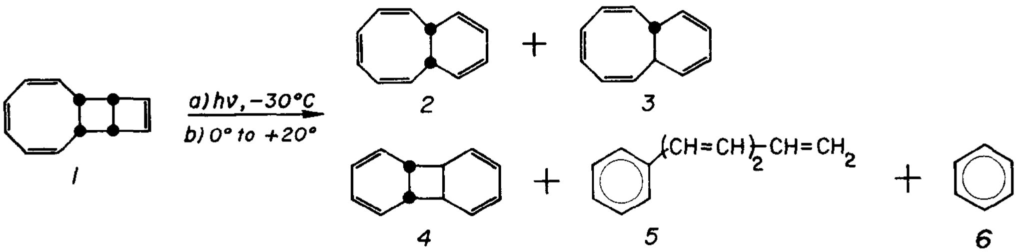
Irradiation of syn-tricyclo[8.2.0.0$^{2.9}$]dodeca-3.5.7.11-tetraene (1) in diethyl ether at -30° C using a low pressure Hg-lamp yields cis- (2) and trans-bicyclo[6.4.0]dodeca-2.4.6.9.11-pentaene (3) together with some anti-tricyclo[6.4.0.0$^{2.7}$]dodeca-3.5.9.11-tetraene (4) 1-phenylhexatriene (5) and benzene (6) 2) :



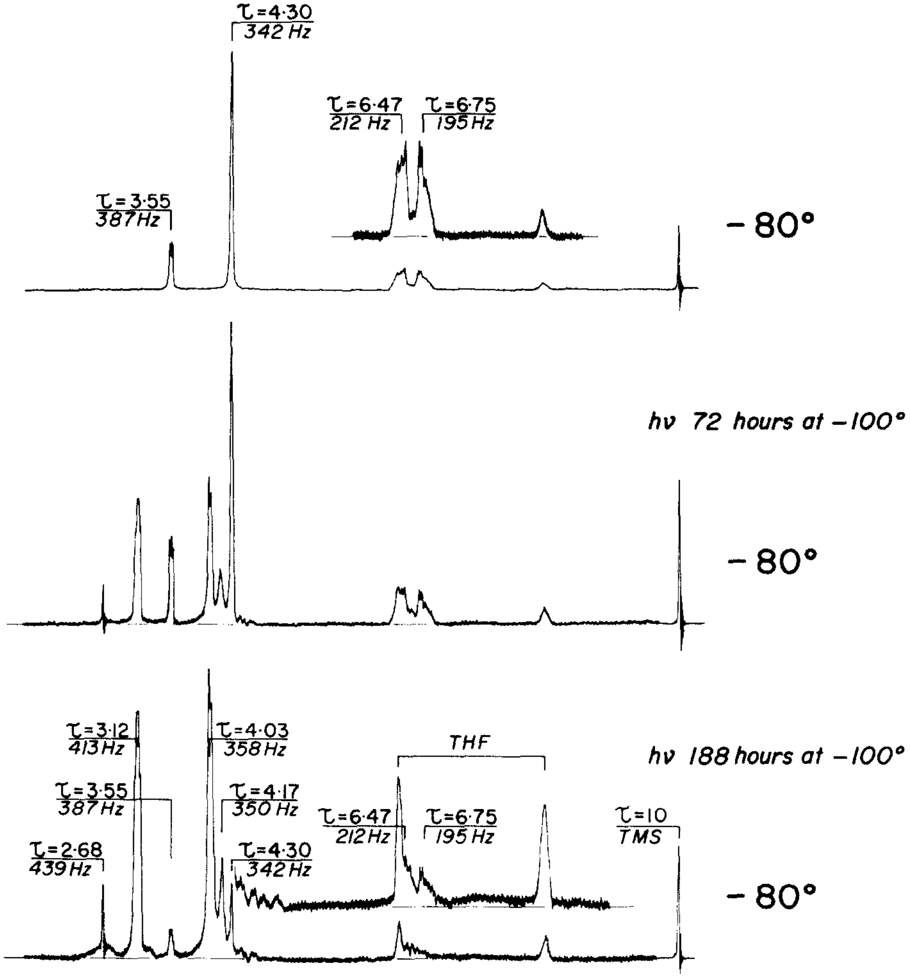
We have proved 2) that 4 and 6 are formed thermally at the expense of 2 while 5 could result from a photochemically induced suprafacial sigmatropic 1-7 H-shift in 2 and/or in 3, followed by an electrocyclic rearrangement.

In order to explain the formation of the bicyclic $C_{12}H_{12}$ hydrocarbons 2 or 3, we have postulated 2) that a very unstable [12]annulene could be formed as a primary product of the photolysis of 1. This [12]annulene could then rearrange thermally or photochemically into 2 or 3 in accordance with the Woodward-Hoffmann rule 3). Such electrocyclic rearrangements would be analogous to those observed with [16]annulene 4).

We now describe the preparation and the properties of the very labile [12]annulene which is formed as the main product when 1, 2 or 3 is irradiated at -100°C.

Irradiation of syn-tricyclo[8.2.0.0$^{2.9}$]dodeca-3.5.7.11-tetraene (1) at -100°C.

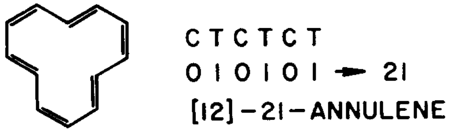
30 mg of 1 5) dissolved in 0.3 ml of THF-d_8 were irradiated in a sealed quartz NMR tube at -100°C 6) using a low pressure Hg-lamp 7). The composition of the solution was followed by NMR spectroscopy (at -80°C or -100°C). The figure shows three characteristic spectra, i.e. the spectrum of 1 before irradiation and after 72 and 188 hours of irradiation.



NMR spectra (60 MHz), recorded at -80°C, of 1 before irradiation and after 72 and 188 hours of irradiation.

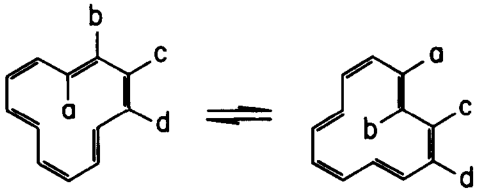
The signals of 1 (τ = 3.55 (2 olefinic cyclobutene H), τ = 4.30 (6 olefinic H), τ = 6.47 and τ = 6.75 (2 sets of 2 bridgehead protons)) decrease progressively in intensity while two new signals of equal intensity develop at τ = 3.12 and τ = 4.03 (two other weak signals also appear : one at τ = 2.68 is due to benzene formed in very small amounts, the other at τ = 4.17 is due to a small quantity of 3 formed). After 188 hours irradiation, the ratio H_{olef}/H_{aliph} of the total NMR intensity between τ = 2.8 and τ = 5.5 (olefinic H) to the intensity of the signals located between τ = 6.0 and τ = 7.5 (aliphatic H, THF contribution deducted) reach the very high value of 16.5. This indicates the formation of a [12]annulene. We attribute the two peaks of equal intensity located at τ = 3.12 and τ = 4.03 to the [12]annulene in which cis and trans double bonds alternate (i.e. to the [12]-21-annulene (7) in our coded notation[8]) :

7

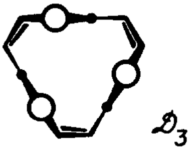


The signal at τ = 4.03 is attributed to the six protons on the cis double bonds while the signal at τ = 3.12 is due to the six protons on the trans double bonds. This attribution is in agreement with the structure proposed, if one assumes

i) either that the following fast conformational mobility is present :



ii) or that only one conformation exists in which all the torsion angles are equal in absolute value and very close to 90°, i.e. a conformation in which the trans double bonds are perpendicular to the mean plane of the molecule ($\mathcal{D}_3$ symmetry) :



In the following publication[9] we report that the NMR spectrum of the [12]-21-annulene is temperature dependent between -170°C and -130°C and that the conformational mobility mentioned above is indeed taking place.

After 188 hours of irradiation, the composition of the solution was estimated from the NMR spectrum to be as follows[10] :

Compound	1	3	5	6	7
Relative amount	12%	~ 5%	~ 5%	~ 7.5%	70%

Solutions containing up to 80% of [12]annulene could be obtained by irradiation of 1 in THF-d_8 at -115° in one single period of 5 days.

A chemical proof for the formation of a [12]annulene on irradiation of 1 was obtained in the following manner :

0.7 g of 1 in 150 ml of ether were irradiated at -80°C ; after addition of 120 ml of precooled ethanol the photolysed solution was submitted to hydrogenation at -70°C using a rhodium catalyst$^{11)}$. 30% of cyclododecane were found in the C_{12} hydrocarbon mixture$^{12)}$.

Thermal rearrangement of the [12]-21-annulene (7).

A rapid thermal rearrangement of the [12]-21-annulene (7) was observed at -40°C and followed by NMR spectroscopy. The signals of 7 (τ = 3.12 and τ = 4.03) disappear fast while new signals attributed to compound 2 (τ = 4.17 and τ = 6.53 $^{2)}$) develop. The ratio H_{olef} to H_{aliph} drops from 16.3 to 7 in one hour and reaches the limiting value of 5.03 already after a few hours. The rate at -40°C of this thermal rearrangement $7 \xrightarrow{\Delta} 2$ and the corresponding free energy of activation were found to be :

$$k_{7 \rightarrow 2}\ (-40^\circ C) = 2.4\ (\pm 0.4) \times 10^{-4} s^{-1} \qquad \Delta G^{\ddagger}\ (-40^\circ C) = 17.4\ (\pm 0.1)\ \text{kcal mole}^{-1}$$

Upon heating at +30°C, 2 disappears rapidly to give cleanly compound 4, which then rearranges into benzene 6 $^{2)}$. That the rearrangements $7 \rightarrow 2$, $2 \rightarrow 4$ and $4 \rightarrow 6$ are clean steps is indicated by the fact that the ratio H_{olef}/H_{aliph} = 16.3 observed for the [12]-21-annulene solution is identical with the ratio H_{arom}/H_{aliph} = 16.4 observed after total conversion of 7 into benzene. The rate constants at +30°C for the reactions $2 \xrightarrow{\Delta} 4$ and $4 \xrightarrow{\Delta} 6$ and the corresponding free energies of activation were estimated as :

$$k_{2 \rightarrow 4}\ (+30^\circ C) = 1.1\ (\pm 0.1) \times 10^{-4} s^{-1} \qquad \Delta G^{\ddagger}\ (+30^\circ C) = 23.3\ (\pm 0.1)\ \text{kcal mole}^{-1}$$

$$k_{4 \rightarrow 6}\ (+30^\circ C) = 1.0\ (\pm 0.1) \times 10^{-5} s^{-1} \qquad \Delta G^{\ddagger}\ (+30^\circ C) = 24.7\ (\pm 0.1)\ \text{kcal mole}^{-1}$$

Irradiation of [12]-21-annulene (7) at -70°C.

A solution of 7 in THF-d_8 was prepared as indicated above ; its composition is given in the table below (1st row). UV irradiation at -70°C (using a low pressure Hg lamp) yields, after 7 days, a mixture containing essentially 2 and/or 3 as indicated in the table (2nd row). In order to evaluate the relative amount of 3 formed$^{13)}$, the tube was kept at +50°C for several hours ; under these conditions 7 and 2 are converted into benzene while 1 and 3 remain unchanged (and 5 polymerizes and precipitates). The composition of the solution after heating is reported in the table (3rd row).

<table>
<tr><th>Compounds</th><th>1</th><th>2</th><th>3</th><th>5</th><th>6</th><th>7</th></tr>
<tr><td>7 at -100°C</td><td>~ 10%</td><td colspan="2">~ 5%</td><td>~ 5%</td><td>~ 5%</td><td>75%</td></tr>
<tr><td>hν 7 days at -70°C</td><td>~ 10%</td><td colspan="2">68%</td><td>~ 5%</td><td>~ 5%</td><td>~12%</td></tr>
<tr><td>Δ 5 hours at +50°C</td><td>~ 10%</td><td>0%</td><td>27%</td><td>0%</td><td>52%</td><td>0%</td></tr>
</table>

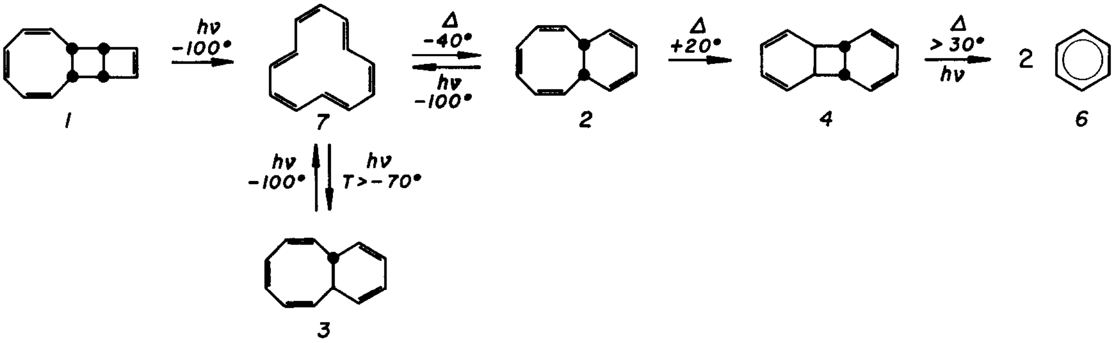
These results indicate that, upon irradiation at -70° under our experimental conditions (7 days), about one third of 7 is converted photochemically into 3, the other two thirds being trans-formed thermally into 2. The rate of the photochemically induced conversion of 7 to 3 is probably temperature dependent because 3 is obtained in higher yield when 1 is irradiated at higher temperatures[2)]. This behaviour would be analogous to the photochemically induced electrocyclic reaction in [16]annulene[4)].

Photolysis of cis- (2) and trans-bicyclo[6.4.0]dodeca-2.4.6.9.11-pentaene (3) at -100°C.

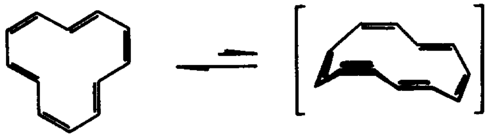
Photolysis of 2 and 3 at -100°C in THF-d_8 using a low pressure Hg-lamp regenerates in good yield (60-75%) [12]-21-annulene (7).

Discussion.

The following scheme summarizes those reaction steps, thermal or photochemical, which have been established experimentally :



The generation of 2 and 3 from 7 and the inverse reactions cannot be understood by a simple application of the Woodward-Hoffmann rule[3)] for electrocyclic reactions; e.g., [12]-21-annulene (7) should produce thermally a bicyclic [6.4.0]dodecapentaene with one trans double bond. But, if one assumes that [12]-21-annulene (7) is in dynamic equilibrium with another configuration containing three consecutive cis double bonds such as, e.g., [12]-5-annulene (7a), then all these reactions can then be readily understood : 7a $\xrightarrow{\Delta}$ 2, 7a $\xrightarrow{h\nu}$ 3 and the inverse reactions 2 $\xrightarrow{h\nu}$ 7a and 3 $\xrightarrow{h\nu}$ 7a are all symmetry allowed[14)].



[12]-21 [12]-5

7 7a

Such a dynamic equilibrium is observed in the case of [16]annulene[8] :

$$[16]\text{-}85 \rightleftharpoons [16]\text{-}91$$

75% 25%

The hypothesis of an analogous behaviour in the case of the [12]annulene is thus reasonable. If such an equilibrium exists, it must lie strongly on the side of the [12]-21 configuration (7) since no NMR signals which could be attributed to another configuration were observed. We may also conclude that among all the possible configurations for a [12]annulene, the 21-configuration must be the most stable one.

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   Angew. Chem., internat. edit., 5, 130 (1966).
6) The thermostat used for irradiation at -100°C consists of a Dewar quartz tube through which a cold N_2 gas stream flows. The temperature of the gas - and thus of the sample - can be maintained constant at ± 0.5° for several days.
7) Low pressure Hg-lamp : Nester and Faust, mod. NFUV-300 with quartz protection sleeve, 300 W, 90% intensity around 2537 Å.
8) J.F.M. Oth and J.-M. Gilles, Tetrahedron Letters, 60, 6259 (1968).
9) J.F.M. Oth, J.-M. Gilles and G. Schröder, Tetrahedron Letters, following publication.
10) The NMR spectra of compounds 1, 2, 3, 4 were recorded in THF as reference spectra. For the preparation and purification of these compounds, cf. ref. 2).
11) S. Masamune and R.T. Seidner, Chem. Comm., 542 (1969).
    H.C. Brown and C.A. Brown, J. Amer. Chem. Soc., 84, 1494 (1962).
12) Cyclododecane was isolated by gas chromatography and identified by comparison of its IR and NMR spectra with those of an authentic sample.
13) 2 and 3 have their NMR signals superimposed.
14) The mechanism outlined in ref. 2 for explaining the formation of 2 and 3 when 1 is photolysed at -30°C has to be modified accordingly.