Thermal Rearrangement of Some 1- and 2-Substituted Azulenes to Naphthalenes

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The products from thermolysis at 440 °C of [2-^{2}H]azulene, 2-[^{13}C]methyl[2-^{13}C]azulene, 1- and 2-cyanoazulene, and 1,2-dimethylazulene are reported. The results, taken with those published previously, show that the migration of C-2 of azulene (together with its attached group) to the α-position of the naphthalene is a general phenomenon, which has occurred in about one-third of the products.

THE thermal rearrangement of azulenes to naphthalenes is catalysed by radicals and probably occurs by rearrangement of radical adducts.[1] Product analysis of thermolyses of azulenes possessing one or more substituents in the seven-membered ring led to proposals [1] that rearrangement results from (i) attack of a radical (R·) on a carbon atom in the seven-membered ring, (ii) migration of the attacked carbon atom and its substituents (*e.g.* CHR or CRMe) into the five-membered ring, and (iii) loss of R, H, or Me to form the naphthalene. However the final disposition of carbon atoms and substituents in the original five-membered ring was not understood, since 2-methylazulene unexpectedly gave 1- as well as 2-methylnaphthalene. The present paper describes the synthesis of 2-[^{13}C]methyl[2-^{13}C]azulene and the analysis of its thermolysis product by ^{13}C n.m.r. The thermolyses of several other azulenes with substituents in the five-membered ring are reported. These serve to establish the generality that 2-X-azulenes give 1- and 2-X-naphthalenes in the ratio *ca.* 1 : 2.

EXPERIMENTAL

3-Acetylcyclohepta[b]*furan-2-one*.—The procedure has been previously described.[2] Sodium hydride (420 mg; 80% suspension in oil) and ethyl acetoacetate (1.86 g) were stirred in benzene (30 ml) cooled in an ice-bath under nitrogen. 2-Chlorotropone [3] (1 g) in benzene (15 ml) was added dropwise over 15 min and the mixture was then stirred at room temperature overnight. It was then shaken with water, and the organic layer was separated, dried, and evaporated. Recrystallisation of the residue from benzene gave yellow crystals (1.1 g, 82%), m.p. 206—207°, δ_C (25 mg ml^{-1}) 30.1 (CH_3), 120.1, 131.8, 135.0, 136.6, and 140.8 (ring CH), 159.1 (lactone C=O), and 195.0 (acetyl C=O).

Cyclohepta[b]*furan-2-one*.[2]—3-Acetylcyclohepta[*b*]furan-2-one (1.1 g) in 75% H_2SO_4 (40 ml) was heated at 120—130 °C

[1] R. W. Alder and G. Whittaker, *J.C.S. Perkin II*, 1975, 714.
[2] S. Seto, *Sci. Reports Tôhoku Univ.*, 1963, (1) **37**, 367 (*Chem. Abs.*, **49**, 8234).
[3] W. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.*, 1952, **74**, 5683.

for 3 h under nitrogen. The solution was diluted to 300 ml with cold water and the pH adjusted to 6 by addition of solid $NaHCO_3$; a dark precipitate formed and was filtered off. The filtrate was extracted with dichloromethane (3 × 50 ml) and the combined extracts were dried and evaporated. Recrystallisation from petroleum (b.p. 80—100°) gave long orange needles (430 mg, 50%), m.p. 69—70°.

3-[$^{13}C_2$]*Acetylcyclohepta*[b]*furan*-2-*one*.—Sodium [$^{13}C_2$]-acetate (80 mg, 1.3 equiv.; 91.69% ^{13}C at C−1, 93.3% at C−2), phosphoryl chloride (120 mg), cyclohepta[*b*]furan-2-one (100 mg), dry 1,2-dichloroethane (6 ml), and, finally, tin(IV) chloride (800 mg) were placed successively in an ampoule, which was then evacuated, sealed, and heated at 100 °C for 20 h. During this time the precipitate and solution changed colour from yellow through green to purple. The mixture was partitioned between aqueous ammonium chloride and dichloromethane and the yellow organic layer was dried and evaporated to give 3-[$^{13}C_2$]acetylcyclohepta[*b*]furan-2-one (123 mg, 94.5%), δ_H 2.6 (3 H, dd, *J* 129 and 6.5 Hz), 7.5 (4 H, m), and 9.2 (1 H, d, *J* 11 Hz), δ_C (25 mg ml^{-1}) 30.1 (d, *J* 42.7 Hz) and 195.0 (d, *J* 42.7 Hz) [natural abundance peaks at 120.0, 131.8, 134.9, 136.5, 140.8, and 159 (all singlets)]; centre peaks between the two large doublets were observed corresponding to singly labelled material.

Sodium 1-*Cyano*-2-[^{13}C]*methyl*[2-^{13}C]*azulene*-3-*carboxylate*.—The procedure has been previously reported.[4] 3-[$^{13}C_2$]-Acetylcyclohepta[*b*]furan-2-one (60 mg) and ethyl cyanoacetate (73.5 mg.) in ethanol (1.4 ml) were stirred at 0 °C and treated with a solution (1.4 ml) of sodium (260 mg) in ethanol (10 ml). The mixture was stirred at room temperature for 3 days, then partitioned between water and dichloromethane, and the aqueous layer was evaporated to dryness. ^{13}C N.m.r. [D_2O soln. (25 mg ml^{-1})] showed two doublets (*J* 44.2 Hz) separated by 138.8 p.p.m. Conversion into the acid by addition of hydrochloric acid to an aqueous solution of the sodium salt gave a pink precipitate, which was filtered off and used directly for the next stage.

2-[^{13}C]*Methyl*[2-^{13}C]*azulene*.—The foregoing acid (60 mg) and 88% phosphoric acid (5 ml) were heated at 110 °C in an evacuated ampoule for 16 h and the product was partitioned between water and dichloromethane. Chromatography of the organic-soluble material on grade IV alumina gave two products; elution with petroleum (b.p. 60—80°) gave 2-methylazulene (20 mg); elution with 20% dichloromethane in petroleum (b.p. 60—80°) gave 1-cyano-2-methylazulene (1 mg). The main product showed δ_H 2.7 (3 H, dd, *J* 126 and 6.5 Hz), 7.0—7.8 (5 H, m), and 8.4 (2 H, d, *J* 10 Hz). ^{13}C N.m.r. (20 mg in 0.8 ml $CDCl_3$; Me_4Si) showed the signals for the enriched carbons at δ_C 16.7 (d, *J* 44.2 Hz) and 150.3 (d) with small centre peaks [natural abundance peaks were observed at 118.2 (d, *J* 54.9 Hz, presumably C-1 and C-3), 123 (s), 134.1 (d, *J* 7.6 Hz, presumably C-4 and C-8), and 135.3 (s)]. ^{13}C N.m.r. of the 1-cyano-2-[^{13}C]methyl[2-^{13}C]azulene showed doublets (*J* 44.2 Hz) at δ_C 15.7 and 153.5. The 2-methylazulene (14 mg) sublimed without leaving a residue. The sublimate had m.p. 50° (lit.,[5] 49—50°) and was sealed in an evacuated 300 ml ampoule for thermolysis.

Diethyl [2-^2H]*Azulene*-1,3-*dicarboxylate*.—(*a*) Diethyl 2-aminoazulene-1,3-dicarboxylate [6] (140 mg) was twice treated with deuterium oxide (1 ml) in acetone (5 ml) and then dissolved in [$^2H_4$]methanol (1 ml). Deuteriosulphuric acid (0.05 ml) and deuterium oxide (1 ml) were added and the mixture was stirred at room temperature while sodium nitrite (70 mg) in deuterium oxide (0.1 ml) was added dropwise. After stirring for 3 days, the mixture was diluted with water (20 ml) and extracted with dichloromethane (2 × 20 ml). The organic-soluble material was chromatographed on alumina (grade IV) in hexane (1 000 : 1 adsorbant–substrate ratio) to give diethyl [2-^2H]azulene-1,3-dicarboxylate (82 mg, 62%), 92% 2-^2H by 100 MHz n.m.r.

(*b*) The amine (190 mg) was treated with deuterium oxide–acetone as in (*a*) and dried under vacuum before dissolution in [$^2H_4$]methanol (2 ml) and deuteriosulphuric acid (0.2 ml). In a dry box nitrosonium tetrafluoroborate (120 mg) and deuteriosulphuric acid (15 drops) were added in portions, and the solution assumed a deep blue ' azulenic ' colour. The mixture was then removed from the dry box and stirred at room temperature for 20 h [deuterium oxide (1 ml) was added after 1 h]. It was then burgundy red in colour and was worked up as in (*a*) to give the product (100 mg, 56%), 83% 2-^2H by n.m.r.

[2-^2H]*Azulene*.—The diester from (*a*) above (82 mg) and KOH (100 mg) in aqueous 75% ethanol (1 ml) were refluxed for 30 min, cooled, and acidified with hydrochloric acid. The pink precipitate was collected by centrifugation and dried. Sublimation of this crude acid at 270—280 °C and 200 mmHg gave [2-^2H]azulene (27 mg, 69%), 91% 2-^2H by n.m.r. Alternatively the crude diacid [from 100 mg of diester from (*b*) above] was refluxed with trifluoroacetic acid (5 ml) under nitrogen for 30 min. Dilution with water and chromatography of the precipitate on alumina (grade IV) with hexane gave [2-^2H]azulene (40 mg, 84%), 83% 2-^2H by n.m.r.

Azulene-1-*carbonitrile*. This was prepared from azulene *via* azulene-1-carbaldehyde and its oxime as described.[7] Recrystallisation from petroleum gave deep red needles, m.p. 54—55°.

Azulene-2-*carbonitrile*. This was prepared from diethyl 2-aminoazulene-1,3-dicarboxylate by literature procedures.[8] Recrystallisation from methanol–water gave blue crystals, m.p. 77—78°.

1,2-*Dimethylazulene*.—Phosphoryl chloride (171 mg, 1.2 equiv.) was added to redistilled dimethylformamide (DMF) (1 ml) at 0 °C. This yellow solution was added to 2-methylazulene (130 mg) in DMF (2 ml) and the mixture stirred at room temperature for 30 min; the blue solution rapidly turned a deep red with concomitant formation of a precipitate. The mixture was diluted with aqueous $NaHCO_3$ (30 ml) and dichloromethane (25 ml) and stirred for 1.5 h; the aqueous solution was then no longer red. Chromatography of the organic-soluble product on grade IV alumina with 1 : 1 ether–petroleum as eluant, followed by recrystallisation from petroleum, gave deep red needles of 2-*methylazulene*-1-*carbaldehyde* (100 mg, 65%), m.p. 92—94° (Found: C, 84.7; H, 5.8. $C_{12}H_{10}O$ requires C, 84.15; H, 6.3%).

This product (50 mg), bis-(2-hydroxyethyl) ether (2 ml), and hydrazine hydrate (0.4 ml) were heated to 185 °C, and KOH (one pellet) was added. The mixture was refluxed for 10 min, cooled, and diluted with dichloromethane (30 ml).

[4] T. Nozoe, K. Takase, T. Nakazawa, and S Fukuda, *Tetrahedron*, 1971, **27**, 3357.

[5] T. Nozoe, S. Seto, and S. Matsumura, *Bull. Chem. Soc. Japan*, 1962, **35**, 1990.

[6] T. Nozoe, S. Seto, S. Matsumura, and Y. Murase, *Bull. Chem. Soc. Japan*, 1962, **35**, 1179.

[7] K. Hafner and C. Bernhard, *Annalen*, 1959, **625**, 108.

[8] P. A. Plattner and J. Wyss, *Helv. Chim. Acta*, 1941, **24**, 483.

Normal work-up and chromatography on grade II alumina with petroleum, followed by sublimation, gave 1,2-dimethylazulene (18 mg, 40%), m.p. 56—58° (lit.,[8] 58—59°).

Thermolysis Procedure.—Ampoules were prepared as described previously [1] and thermolyses conducted at 440 ± 3 °C as before in the oven of a Perkin-Elmer F11 gas chromatograph.

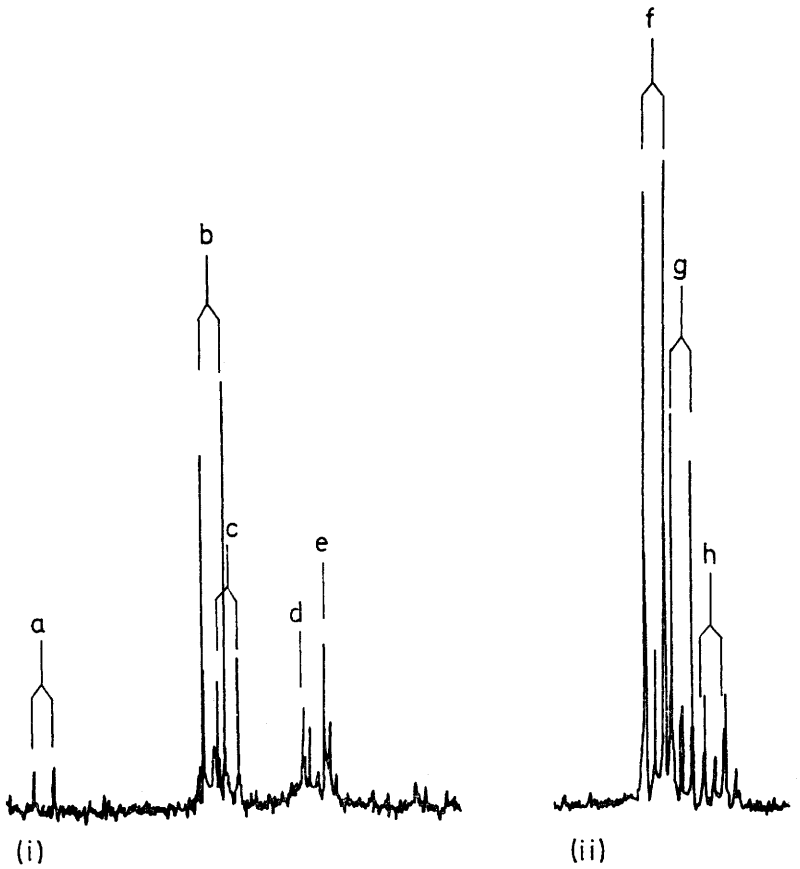
Product Analysis.—Products of azulene and methylazulene thermolyses were analysed on capillary and support-coated open tubular columns with MBM stationary phase as described previously.[1] Azulenecarbonitrile thermolyses were analysed on a 15 m support-coated open tubular column with Apiezon L stationary phase at 200 °C.

^{13}C N.m.r. spectra were recorded at 25.1 MHz on a JEOL JNM PS 100 FT spectrometer for solutions in $CDCl_3$ unless otherwise stated, with Me_4Si as internal standard.

ratio of α- to β-protons. Raman spectra of this product and of [1-^{2}H]- and [2-^{2}H]-naphthalene (prepared from the bromonaphthalenes) were performed on a Coderg T800 spectrometer using a Coherent Radiation 52G argon laser with excitation at 514.5 nm. The relative ε values of the 870 cm^{-1} band due to [1-^{2}H]naphthalene and the 887 cm^{-1} band due to the [2-^{2}H]-isomer were 3.87 : 1 (naphthalene itself does not absorb significantly at either point). The ratio of bands for the thermolysis product was 1.59 : 1 and thus the 1- to 2-^{2}H ratio was 1 : 2.4.

RESULTS

2-[^{13}C]*Methyl*[2-^{13}C]*azulene.*—Thermolysis of a 13 mg sample in a 300 ml ampoule for 4 h at 440 °C gave a product mixture which was similar to that reported earlier [1] for the



^{13}C N.m.r. spectrum of thermolysis product of 2-[^{13}C]methyl[2-^{13}C]azulene: (i) aromatic region; (ii) methyl region. Peak assignments: (a) doublet (*J* 44 Hz) centred at δ_C 150.3, 2-^{13}C of 2-[^{13}C]methyl[2-^{13}C]azulene, (b) doublet (*J* 44 Hz) centred at 135.4, 2-^{13}C of 2-[^{13}C]methyl[2-^{13}C]naphthalene, (c) doublet (*J* 44 Hz) centred at 134.2, 1-^{13}C of 1-[^{13}C]methyl[1-^{13}C]naphthalene, (d) singlet at 127.8, 1-^{13}C of [1-^{13}C]naphthalene, (e) singlet at 125.8, 2-^{13}C of [2-^{13}C]naphthalene, (f) doublet centred at 21.7, 2-[^{13}C]methyl of the 2-methylnaphthalene, (g) doublet centred at 19.4 1-[^{13}C]methyl of the 1-methylnaphthalene, and (h) doublet centred at 16.7, 2-[^{13}C]methyl of the 2-methylazulene

Analysis of the product from [2-^{2}H]azulene by Raman spectroscopy was conducted as follows. Thermolysis of a 20 mg sample for 8 h at 440 °C gave 96% conversion into naphthalene (by g.l.c.). A solution of the product in hexane was shaken repeatedly with 85% orthophosphoric acid until no further darkening of the acid layer was noticeable. The organic layer was then washed with water, dried [Na_2CO_3], and evaporated. Sublimation gave naphthalene (9 mg); ^{1}H n.m.r. showed an approximately 1 : 1 unlabelled compound (96% conversion; products contain 5.3% naphthalene, 23.5% 1- and 55.1% 2-methylnaphthalene, 4.7% 1,2-, 1.9% 1,3-, and 2.0% 2,3-dimethylnaphthalene, and 1.5% azulene). The ^{13}C n.m.r. spectrum of this product (10 mg) is shown in the Figure, together with peak assignments made on the basis of natural abundance spectra of the known components. Natural abundance spectra were obtained at much higher concentrations and, as may be expected, chemical shifts are concentration-

dependent. Shifts were extrapolated to infinite dilution, but even so, it has not proved possible to assign unambiguously the several observable doublets in both (a) and (b) regions of the spectrum to the dimethylnaphthalenes known to be present. Examination of the peaks at the centre of the main doublets shows that for both the 1- and 2-methylnaphthalenes not more than about 3% of each product has the ring and methyl ^{13}C labels separated (allowing for the known proportion of singly-labelled material). The minor product naphthalene is seen to be a mixture of [1-^{13}C]- and [2-^{13}C]-isomers in an apparent ratio of *ca.* 1 : 2.

Examination of the thermolysis product by g.l.c.–mass spectrometry showed that the dimethylnaphthalene isomers formed largely contained three ^{13}C atoms, as expected.

[2-^{2}H]*Azulene*.—A 20 mg sample was thermolysed for 8 h at 440 °C, to ensure a high conversion into naphthalene (96%). Proton n.m.r. spectra proved an insufficiently accurate method of product analysis and several other analytical methods (^{2}H n.m.r. and i.r. spectra, and conversion into 1-bromonaphthalene followed by mass spectral analysis) were tried before it was found that Raman spectra provided a convenient answer (see Experimental section).

Azulene-1- *and* 2-*carbonitrile*.—Thermolysis of the 1-isomer for 2 h at 440 °C gave only 6% conversion; thus this compound rearranges more slowly than any other azulene we have examined to date. Thermolysis of 5.5 mg in a 55 ml ampoule for 16 h at 440 °C gave a 78.8% conversion, and a product consisting of 1.6% naphthalene and 65.3% 1- and 33.0% 2-naphthonitrile. Azulene-2-carbonitrile was thermolysed at a normal rate (75.8% conversion in 2 h at 440 °C) and the product consisted of 0.8% naphthalene, 29.7% 1- and 67.9% 2-naphthonitrile, and 1.6% azulene-1-carbonitrile. Co-thermolysis of 5 mg each of azulene-1- and 2-carbonitrile in a 100 ml ampoule for 2 h gave a product mixture which consisted of 10% 1- and 12% 2-naphthonitrile, 42% azulene-1-carbonitrile, and 36% azulene-2-carbonitrile. Thus in a co-thermolysis, azulene-2-carbonitrile disappears more slowly than when thermolysed alone.

1,2-*Dimethylazulene*.—Thermolysis under standard conditions (10 mg in 100 ml ampoule for 2 h at 440 °C) gave the products shown in Table 1, which also shows the previously reported figures for 1,3-dimethylazulene.[1]

TABLE 1

Thermolyses of 1,2- and 1,3-dimethylazulenes

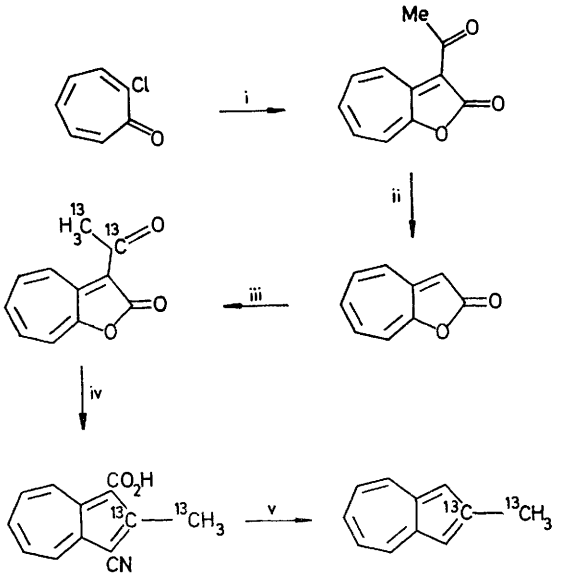
	% Conversion	N	1MN [a]	2MN	1,2-DMN	1,3-DMN	1,4-DMN	2,3-DMN	Unknown TMNs	1MA	2MA	A	1,2-DMA
1,2-DMA [a]	86.9	0.4	4.1	5.9	45.9	12.5	0.5	16.4	14.1			0.2	
1,3-DMA	83.7		2.0	1.6	1.2	54.9	26.2		11.8	0.7	0.4		1.2

[a] DMA = dimethylazulene, MN = methylnaphthalene, *etc.*

DISCUSSION

2-[^{13}C]Methyl[2-^{13}C]azulene was synthesised by the route set out in the Scheme. The only novel feature is the re-acetylation of cyclohepta[*b*]furan-2-one, which we found could be achieved in good yield with acetyl chloride and an excess of tin(IV) chloride. The starting lactone is probably unusually basic and the requirement for an excess of tin(IV) chloride may indicate that the acetyl chloride–tin chloride complex attacks, not the free lactone, but its tin chloride complex. The isolation of [$^{13}C_2$]acetic acid and/or [$^{13}C_2$]acetyl chloride was avoided by *in situ* conversion of sodium acetate into acetyl chloride by phosphoryl chloride. Thionyl chloride proved unsuitable.

The remaining syntheses followed literature precedents closely with the exception of the reductive deamination used to introduce the 2-^{2}H. McDonald and Richmond [9] recently reported the reductive deamination of the azulenylamine in question in quantitative yield by using hydroquinone in dioxan. We repeated their preparation using pre-exchanged amine, $C_6H_4(O^2H)_2$, and deuteriosulphuric acid, and were surprised to obtain a product with essentially no deuterium at position 2. It is possible that the hydrogen is provided by the aromatic protons of hydroquinone, but a more likely source, in our opinion, is the solvent dioxan. Cadogan and Molina [10] have reported this to be an effective reducing agent for diazonium ions. Subsequent study showed that our azulenylamine could be reduced with methanol, ethanol, or propan-2-ol (in increasing order of effectiveness); we eventually used [$^{2}H_4$]methanol as a convenient source of deuterium. The final step in this synthesis, decarboxylation of [2-^{2}H]azulene-1,3-dicarboxylic acid, is more efficiently performed by brief



Reagents: i, MeCO·C̄H·CO$_2$Et Na$^+$, PhH; ii, 75% H_2SO_4, 120—130 °C, 3 h; iii, $^{13}CH_3$·$^{13}CO_2Na$, $POCl_3$, $SnCl_4$, $(CH_2Cl)_2$; iv, NC·C̄H·CO$_2$Et Na$^+$, EtOH; v, 85% H_3PO_4, 110 °C, 16 h

[9] R. N. McDonald and J. M. Richmond, *J.C.S. Chem. Comm.*, 1973, 605.

[10] J. I. G. Cadogan and G. A. Molina, *J.C.S. Perkin I*, 1973, 541.

refluxing in trifluoroacetic acid, than by the previously reported thermolytic procedure.

The ^{13}C n.m.r. spectrum of the thermolysis product from 2-[^{13}C]methyl[2-^{13}C]azulene (see Figure) proves that, under the conditions used, the two labelled carbons do not become separated in either major product. For the 1-methylnaphthalene this requires some ring rotation or transposition during rearrangement. This result rules out several possible mechanisms for this remarkable rearrangement but leaves open numerous other possibilities.

In our first attempt to thermolyse the doubly-labelled compound, material was taken directly from a $CDCl_3$ solution and placed in the ampoule without sublimation. Subsequent thermolysis gave a poor recovery and a tarry product in which the ratio of 1- to 2-methylnaphthalene was 1 : 7 (not 1 : 2 as usual). ^{13}C N.m.r. data for this product showed that in about one-half of the small amount of 1-methylnaphthalene obtained, the two labels had become separated. This result, obtained with inadequately purified material, should not be ignored in view of previous unsuccessful attempts to change the 1- to 2-methylnaphthalene ratio by alteration of the thermolysis conditions. Possibly the impurities diverted or trapped an intermediate on the route to the 1-methyl isomer.

The Figure shows the presence of both [1-^{13}C]- and [2-^{13}C]-naphthalene. We have previously argued [1] that the naphthalene produced in this thermolysis arises from azulene produced by demethylation of 2-methylazulene. If this is so, then we note the *ca.* 1 : 2 ratio of α- to β-^{13}C peaks observed. All the other azulenes substituted or labelled in the 2-position give substituted or labelled naphthalenes with an α : β ratio of 1 : 2.3 (see Table 2). 1-Substituted azulenes give an α : β ratio of *ca.* 1 : 0.5. It seems reasonable that these ratios reflect ring permutation possibilities [11] which are intrinsic to the mechanism and which are more or less insensitive to substitution. If this is correct it is interesting to extend the argument by also considering the results for 1,2- and 1,3-dimethylazulenes (Tables 1 and 2).

Let us suppose that the ring which is expanded on rearranging azulene to naphthalene is made up of C-1 to C-3 of azulene (A, B, and C) and one carbon atom from the seven-membered ring (X) and that the bridgehead carbons are unchanged. There are then twelve possible permutations (ignoring the difference between ABCX and XCBA) for C-1—C-4 of naphthalene:

TABLE 2

Major products from thermolyses of five-membered-ring-substituted azulenes

Azulene	Major naphthalene products	Ratio
1-CH_3	1-CH_3, 2-CH_3	1 : 0.49
1-CN	1-CN, 2-CN	1 : 0.51
[2-^2H]	[1-^2H, 2-^2H]	1 : 2.4
[2-^{13}C]	[1-^{13}C, 2-^{13}C]	*ca.* 1 : 2
2-CH_3	1-CH_3, 2-CH_3	1 : 2.32
2-[^{13}C]CH_3-[2-^{13}C]	1-[^{13}C]CH_3-[1-^{13}C], 2-[^{13}C]CH_3-[2-^{13}C]	1 : 2.34
2-CN	1-CN, 2-CN	1 : 2.29
1,2-$(CH_3)_2$	1,2-, 1,3-, and 2,3-$(CH_3)_2$	1 : 0.27 : 0.36
1,3-$(CH_3)_2$	1,3- and 1,4-$(CH_3)_2$	1 : 0.48

(i) ABCX	(v) ACBX	(ix) BACX
(ii) ABXC	(vi) ACXB	(x) BAXC
(iii) AXBC	(vii) AXCB	(xi) BXAC
(iv) XABC	(viii) XACB	(xii) XBAC

The results for 2-substituted azulenes *demand* the occurrence of one or more of the permutations (vi)—(xi). The results for 1,2-dimethylazulene seem to *exclude* (vi), (vii), (x), and (xi), while those for 1,3-dimethylazulene *exclude* (vi), (viii), (ix), and (xi). Thus we have an impasse and one or more of the assumptions made above is wrong. Perhaps substituents do influence the permutations or, in the 1- and 3-positions, they may block certain transpositions or become separated from C-1 or C-3. It is also clear that the real fate of the bridgehead carbons of azulene must be investigated; suitable experiments are in hand. Finally, speculation on mechanisms must await proper unravelling of the transpositional possibilities. [11]

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[11] J. A. Barltrop and A. C. Day, *J.C.S. Chem. Comm.*, 1975, 177.