The Thermal Rearrangements of Azulenes to Naphthalenes

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The rearrangements of azulenes to naphthalenes, which occur at 350—450°, are catalysed by methyl radicals and it is suggested that skeletal rearrangement takes place in radical adducts (*e.g.* $RC_{10}H_8$· from azulene itself). Detailed analysis is reported of the products of thermolyses of the five methylazulenes, of seven dimethylazulenes, of benz-[*a*]- and -[*f*]-azulenes, and of dimethyl azulene-4,5-dicarboxylate and the derived anhydride and *N*-methylimide. The majority of the products can be accounted for by proposing that rearrangement results from (i) attack of a radical (R·) on a carbon in the seven-membered ring, (ii) migration of the attacked carbon 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 products. However the final disposition of carbons and substituents in the former five-membered ring is not understood (2-methylazulene unexpectedly produces 1- as well as 2-methylnaphthalene).

THE rearrangement of azulene (A) to naphthalene (N) on heating was first reported in 1947,[1] although rearrangements occurring during the dehydrogenation of hydroazulenic sesquiterpenoids and leading to naphthalenes had been reported much earlier. This clean thermal rearrangement of a non-alternant aromatic hydrocarbon to an alternant isomer is a unique reaction. The driving force is clear (ΔH_f^0 308 for azulene, 151 kJ mol^{-1} for naphthalene) and the reaction is, of course, highly counterproductive in a preparative sense. Nevertheless, the reaction poses a very interesting problem, since it is not easy to propose *any* reasonable mechanism which has any precedents.

Heilbronner and Kallen [2] have made a kinetic study of the rearrangement of azulene itself. They concluded, quite tentatively, that the reaction might be essentially unimolecular and homogeneous, with E_a *ca.* 200 kJ mol^{-1}. The standard heat of formation of the transition state would therefore be *ca.* 510 kJ mol^{-1}, a very interesting figure, since the heat of formation of the first excited singlet state of azulene is 488 kJ mol^{-1} and that of naphthalene is 528 kJ mol^{-1}. The photochemical conversion of azulene to naphthalene has been reported,[3] though the quantum yield is very low (*ca.* 10^{-5}). From another point of view, however, the reported activation energy is disturbingly low, since no simple bond-switch mechanism is allowed, and from thermochemical estimation, very few stable or potentially stable $C_{10}H_8$ isomers are likely to have heats of formation of <510 kJ mol^{-1}.

Kallen and Heilbronner found a kinetic order of 1·22 under their typical reaction conditions, which unfortunately involved fairly high vapour concentrations of 1—10 g l^{-1}. Under these conditions a brown deposit is formed on the walls of the reaction vessel, although final yields of naphthalene are usually $>85\%$. This brown deposit was found to accelerate the reaction and Kallen also reported that the reaction was modestly accelerated by an increase in the specific surface area of the reaction vessel. Finally, one substituted azulene, 2-methylazulene (2-MA), was studied, and found to give naphthalene (4%), 1- (34%) and 2-methylnaphthalene (1- and 2-MN) (57%), and azulene (5%). The formation of naphthalene and azulene is notable, but the appearance of 1-methylnaphthalene in substantial amounts is perhaps more significant, since this product must be the result of a complex rearrangement. However it was not reported whether recovered methylazulene was rearranged to, for example, 1-methylazulene. A number of examples of rearrangement of 1-substituted azulenes to 2-substituted isomers have been recorded,[4] usually under heterogeneous conditions, and in one case (1-phenylazulene) the reaction is reversible.[5]

EXPERIMENTAL

M.p.s are uncorrected. Mass spectra were taken on an A.E.I. MS902 at 70 eV. N.m.r. spectra were recorded at 25° on a Varian HA100 spectrometer with $CDCl_3$ as solvent. U.v.–visible spectra were recorded on a Pye–Unicam SP 800A spectrophotometer. Alumina for chromatography refers to B.D.H. aluminium oxide, Brockmann activity 2. Diglyme (bis-2-methoxyethyl ether) was purified by distillation, b.p. 62° at 17 mmHg, after standing for several days over sodium wire.

Naphthalenes, etc., *for G.l.c. Standards*.—The 10 dimethylnaphthalenes were commercial samples. All other compounds required as g.l.c. standards were prepared by published procedures and had b.p.s or m.p.s in close agreement with published values and appropriate i.r. and n.m.r. spectra. Each was pure by g.l.c. on the column specified (see product analysis section).

Synthesis of Azulenes.—(A) *Synthesis of all possible azulenes with one or two methyl groups in the seven-membered ring*. These were prepared by a modified Ziegler–Hafner method. A molar solution of sodium cyclopentadienide in diglyme was prepared from sodium sand and cyclopentadiene according to the procedure of King and Stone.[6] The appropriate methyl- or dimethyl-substituted *N*-methylpyridinium iodide (0·05 mol) was added with stirring to this solution (100 ml) under nitrogen. The salt dissolved within 15 min and the deep red solution was stirred for 24 h. The solution was then heated to 80° for 3 h (evolution of methylamine was sometimes detected). Diglyme was

[1] E. Heilbronner, P. A. Plattner, and K. Wieland, *Experientia*, 1947, **3**, 70; E. Heilbronner and K. Wieland, *Helv. Chim. Acta*, 1947, **30**, 947.

[2] (*a*) H. J. Kallen, Dissertation No. 2856, Eidgenossischen Technischen Hochschule, Zurich, 1958; (*b*) E. Heilbronner in 'Non-benzenoid Aromatic Compounds,' ed. D. Ginsberg, Wiley–Interscience, New York, 1959.

[3] J. Olmsted, *Mol. Photochem.*, 1969, **1**, 331; M. Comtet and H. D. Mettee, *ibid.*, 1970, **2**, 63.

[4] P. A. Plattner, *Helv. Chim. Acta*, 1941, **24**, 283E.

[5] P. A. Plattner, quoted in ref. 2*b*.

[6] R. B. King and F. G. A. Stone, *Inorg. Synth.*, 1963, **7**, 99.

removed under reduced pressure and the residue taken up in ethane-1,2-diol. The azulene was co-distilled with ethane-1,2-diol and extracted from the distillate with light petroleum (b.p. 40—60°). Purification of the azulene normally involved extraction into 88% phosphoric acid, dilution of the acid with ice–water, and re-extraction of the azulene into light petroleum. The 1 : 1 complex with 1,3,5-trinitrobenzene was prepared, recrystallised from methanol, and decomposed by chromatography on alumina, the azulene being eluted with light petroleum (b.p. 30—40°). Solid azulenes were then recrystallised from methanol, followed by sublimation at 90° at water-pump pressure. The stability of the azulenes varied considerably and this sometimes resulted in modified purification procedures being used. It was observed that those azulenes substituted in the 5- and 7-positions gave the lowest yields and were the most difficult to purify; acid extraction of 5,7-dimethylazulene resulted in rapid and complete decomposition, so this step was omitted in this case. Yields quoted in Table 1 are after complete purification.

TABLE 1

Yields and products from the modified Ziegler–Hafner synthesis

Azulene	Yield (%)	M.p. (°C)	Ref.
4-Methyl	1·0		*a*
5-Methyl	0·8	26	*a*
6-Methyl	6·4	82—83	*a*
4,5-Dimethyl	0·2		*b*
4,6-Dimethyl	41		*a*
4,7-Dimethyl	1·7		*c*
4,8-Dimethyl	3·5	68—69	*a*
5,6-Dimethyl	12·0	81—82	*d*
5,7-Dimethyl	1·6	31·5—33·5	

[a] M. Gordon, *Chem. Rev.*, 1952, **50**, 127. [b] W. Herz and J. L. Rogers, *J. Amer. Chem. Soc.*, 1953, **75**, 4498. [c] R. Klimke and W. Treibs, *Annalen*, 1956, **598**, 46. [d] Ref. 9.

The purity of the azulenes was checked by g.l.c. and all gave only one peak on a column (the 100 m capillary column; see product analysis section) which separated all the isomers we had available. 100 MHz N.m.r. spectra ($CDCl_3$ solution) confirmed the expected structures and are tabulated in Supplementary Publication No. SUP 21316 (4 pp.).* Azulenes were stored in the dark at 0° in glass-stoppered sample tubes and were never exposed to sunlight.

(B) *2-Methylazulene.*[7] 2-Methylindane (38·4 g) was heated to 130° (oil-bath) and treated with ethyl diazoacetate (20 g) added dropwise with stirring over 1 h. The temperature was slowly raised to 160° and then kept steady for 3 h. Vacuum distillation of the resulting brown oil yielded 2-methylindane (30 g) and a viscous residue. The recovered 2-methylindane was treated with ethyl diazoacetate (15 g) as above; distillation on this occasion yielded 2-methylindane (22 g). The combined ester residues, dissolved in ethanol (50 ml), were refluxed with sodium hydroxide (21 g) in water (20 ml) overnight. After work-up a viscous acid fraction (8 g, 23%) was obtained on distillation, b.p. 160—164 °C at 12 mmHg.

The acid was then taken up in dichloromethane (10 ml) and 10% palladium on charcoal added with swirling. The solvent was removed and the intimate mixture of acid and dehydrogenating catalyst was then heated gently under nitrogen with a micro-burner until a permanent blue colour appeared. The residue was taken up in ether and placed in a 500 ml flask together with ethane-1,2-diol (200 ml). Distillation was accompanied by co-distillation of 2-methylazulene and was continued until the material distilling was no longer blue. The distillate was extracted with light petroleum (b.p. 60—80°; 2 × 150 ml) and the blue extract treated with 60% H_2SO_4 (200 ml). The resulting yellow-orange acid layer was poured onto ice (800 g) and the azulene re-extracted into light petroleum (2 × 150 ml). The blue solution was then washed with water (2 × 100 ml), dried, and the solvent removed to yield a blue-violet residue. The crude azulene was purified by chromatography on alumina with light petroleum (b.p. 30—40°) as eluant, followed by sublimation at 90° and 14 mmHg. 2-Methylazulene was obtained as violet-blue crystals (0·09 g, 3%), m.p. 47—48°.

(C) *Benz*[a]*azulene.*[8,†] The following procedure was performed simultaneously in duplicate. Fluorene (50 g) was heated to 140° in an oil-bath and ethyl diazoacetate (7 g) added dropwise with vigorous stirring. The temperature was then slowly raised to 165° and held at this value for 2 h. After cooling the procedure was then repeated with further ethyl diazoacetate (7 g). When cold, the green-brown residue was taken up in the minimum of boiling ethanol which, on cooling, caused the excess of fluorene to precipitate out. The solution was filtered and the filtrate stored while the recovered fluorene was dried and then recycled through an identical procedure using ethyl diazoacetate (2 × 5 g). The ethanolic filtrates from all these runs, together with those from the duplicate procedures, were combined and concentrated to 300 ml and again filtered to remove excess of fluorene. The green filtrate was then saponified with NaOH (15 g) in water (20 ml) under reflux for 2 h. The solvent was then removed and the brown deposit taken up in the minimum amount of water and extracted with toluene (2 × 150 ml) to remove the last traces of fluorene. The aqueous solution was then acidified with concentrated HCl and the mixture extracted with toluene (3 × 300 ml). The organic layer, containing dihydrobenz[*a*]azulenecarboxylic acids, was washed with dilute HCl, dried, and the solvent removed, leaving a dark brown residue (8·5 g). This was taken up in a minimum of dichloromethane, divided into three portions, and 10% palladium on charcoal (0·5 g) added to each. Solvent was then removed and the mixtures gently distilled, under nitrogen, using a free flame. The blue distillates were combined and purified by co-distillation with ethane-1,2-diol, extraction into 88% phosphoric acid, chromatography on alumina, recrystallisation from ethanol and sublimation at 100° and 0·1 mmHg to yield *benz*[a]*azulene* as dark green-blue crystals (164 mg), m.p. 189—190° (Found: C, 94·1; H, 5·65%; *m/e*, 178. $C_{14}H_{10}$ requires C, 94·34; H, 5·66%; *M*, 178), τ ($CDCl_3$) 2·69 (1H, s) and 1·60—3·30 (9H, complex m), $\lambda_{max.}$ (MeOH) 248 (log ε 4·00),

* For details of Supplementary Publications see *J.C.S. Perkin II*, 1974, Index issue. Items less than 10 pp. are supplied as full-size copies.

† In our hands the procedure of Treibs *et al.* leads to material, m.p. 210—220°, *m/e* 342 (M^+). The n.m.r. spectrum, in addition to a complex multiplet for 17 aromatic protons, shows a singlet (1H) at τ 4·35. We believe this material is a benz[*a*]-azulene with a fluorenyl substituent.

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

[8] P. A. Plattner, A. Fürst, J. Chopin, and G. Winteler, *Helv. Chim. Acta*, 1948, **31**, 501; the properties reported for benz[*a*]-azulene are rather variable, *e.g.* m.p. 176—177 (J. R. Nunn and W. S. Rapson, *J. Chem. Soc.*, 1949, 825); 192 (W. Treibs, M. Quarg, and E. J. Poppe, *Annalen*, 1956, **598**, 32); or 220° (W. Treibs, *Naturwiss.*, 1946, **33**, 371).

298 (4·73), 307 (4·70), 320 (4·34), 346 (3·43), 383 (3·66), 404 (3·36), 563 (2·48), 622 (2·52), and 688 nm (2·37).

(D) *Benz*[f]*azulene*. This was prepared by the procedure of Muth *et al.*[9] with slight modifications. The product was purified by chromatography on alumina, recrystallisation from methanol, and sublimation at 100° and 0·05 mmHg, to give blue *crystals* (0·5%), m.p. 162—163° (Found: C, 94·4; H, 5·9%; *m/e*, 178), τ ($CDCl_3$) 1·68 (1H, s) and 2·0—2·9 (9H, complex m), $\lambda_{max.}$ (MeOH) 252 (log ε 4·50), 287 (4·75), 341 (3·47), 354 (3·55), 369 (3·51), and 389 nm (3·22).

(E) *Dimethyl azulene-4,5-dicarboxylate, azulene-4,5-dicarboxylic anhydride, and N-methylazulene-4,5-dicarboximide*. These were prepared as described elsewhere.[10]

Thermolysis Procedures.—The standard procedure for thermolysis was the following. Ampoules of *ca.* 100 ml internal volume were fashioned from 20 × 3 cm, thick-walled Pyrex boiling tubes. Before use they were thoroughly soaked in chromic acid, rinsed, and soaked in a sodium hydrogen carbonate solution, washed with distilled water, then acetone, and flame-dried under vacuum. The azulene (10 mg) was then introduced and the ampoule evacuated to 0·05 mmHg with cooling of the contents in solid CO_2–acetone. The ampoule was then sealed and suspended in the oven of a Perkin-Elmer F11 gas chromatograph which had been heated previously to 440°. Temperature stability was always better than ±3°. The standard thermolysis time of 2 h was measured from the time when the temperature read-out indicated 440° again, *ca.* 3 min after introduction of the sample.

Modifications of these standard conditions included the use of 700 ml capacity ampoules, made from drawn-out Pyrex round-bottomed flasks. Ampoule surface activity was altered by omitting the sodium hydrogen carbonate soaking, by treatment with 5% trimethylsilyl chloride in benzene, and by silvering the internal surface by repeated interaction of Tollen's reagent and acetaldehyde, followed by vigorous washing and drying. The surface area of the ampoule was increased by packing it with glass wool.

Thermolyses were also undertaken in the presence of known quantities of benzene, naphthalene, 2,6-dimethylnaphthalene, and azulene. These additives were introduced in quantities calculated, using the ideal gas laws, to exert not greater than one atmosphere pressure at the thermolysis temperature. Thermolysis in the presence of argon was achieved by allowing the evacuated azulene-containing ampoule (125 ml including fittings) to equilibrate at room temperature with a vessel of 92·5 ml capacity containing argon at atmospheric pressure. The ampoule was then sealed, thus containing argon at 0·425 atmospheres at 25°, which corresponds to *ca.* 1 atmosphere at 440°.

Azomethane (50 mg) (obtained from *sym*-dimethylhydrazine by oxidation with mercuric oxide [11] and dried over phosphorus pentoxide) was accurately weighed in a cold receptacle and allowed to volatilise into an evacuated 1·5 l flask. A sample (10 ml) of this gas was then isolated and opened to the evacuated azulene-containing ampoule. This was cooled in liquid nitrogen and sealed, thereby containing azulene (10 mg) and azomethane (*ca.* 0·34 mg).

Product Analysis.—After thermolysis the ampoules were cooled, broken open, and the contents extracted with an appropriate pure solvent. The solutions were evaporated into small pre-weighed, glass-stoppered tubes (standard plastic vial stoppers rapidly turn blue in the presence of azulene). Reweighing showed that recovery of non-volatile, soluble material was almost always >90%, typically 98%. T.l.c. analysis indicated a mixture of starting azulene and naphthalenic isomers, and no decomposition or polymerisation products were detected except in the case of dimethyl azulene-4,5-dicarboxylate.

G.l.c. analyses were performed using a Perkin-Elmer F11 machine equipped with a flame ionisation detector. Response factors for the various azulene and naphthalene isomers were shown to be equal within ±3%, peak areas being measured as the product of retention time and peak height, retention time being measured from the coal-gas peak. Quoted product percentages are mean values calculated from at least four product analyses.

The complex mixtures resulting from rearrangement of mono- or di-methylazulenes were analysed on a 100 m × 0·25 mm stainless steel capillary column coated with *m*-bis-(*m*-phenoxyphenoxy)benzene (MBM) as described by Walker and Ahlberg.[12] Operating at 160° with a helium carrier gas flow rate of 1·7 ml min^{-1}, injection port temperature 250°, and splitter ratio of *ca.* 100 : 1, we obtained efficiencies of better than 100,000 theoretical plates. This resulted in excellent resolution of all the available methyl- and dimethyl-azulenes, and workable resolution of all ten dimethylnaphthalenes except the 2,6- and 2,7-isomers.

Where possible results from this capillary column were checked with a 15 m support-coated, open, tubular column with MBM stationary phase. Operation at 160°, nitrogen carrier gas flow rate of 2 ml min^{-1}, injection port temperature 250°, and splitter ratio 3 : 1 gave typically 10,000 theoretical plates. This gave good resolution of the methylazulenes but only limited resolution of the dimethylnaphthalenes. Where no appreciable overlap of peaks occurred in a given product mixture, isomer percentages calculated from runs on this and the capillary column were not significantly different.

Even with the capillary column some peak overlap occurred between methylazulenes and dimethylnaphthalenes and between dimethylazulenes and the presumed trimethylnaphthalenes. However this problem was easily resolved by rechromatography after extracting the azulenes with 88% phosphoric acid. The retention times of the methyl-azulenes and -naphthalenes are recorded in SUP 21316.

Peak shapes were symmetrical in all cases.

Products from the thermolysis of the benzazulenes were analysed on a 15 m support-coated, open, tubular column with an OV-1 stationary phase operating at 180°, injection port temperature 250°, splitter ratio 3 : 1, and nitrogen carrier gas flow rate of 2·7 ml min^{-1}.

Products from thermolysis of dimethyl azulene-4,5-dicarboxylate were analysed on a 2 m packed column of 25% silicone oil on 60—80 mesh Diatoport S support. Operation at 170°, injection port temperature 250°, and nitrogen carrier gas flow rate of 25 ml min^{-1} gave rise to an efficiency of *ca.* 4000 theoretical plates. This afforded adequate resolution of the starting ester, and the expected major products, dimethyl naphthalene-1,2-, -1,8-, and -2,3-dicarboxylates.

[9] C. W. Muth, M. L. de Matte, A. R. Urbanik, and W. G. Isner, *J. Org. Chem.*, 1966, **31**, 3013.
[10] R. W. Alder and G. Whittaker, *Chem. Comm.*, 1971, 776; *J.C.S. Perkin I*, in preparation.
[11] R. Renaud and L. C. Leitch, *Canad. J. Chem.*, 1954, **32**, 545.
[12] J. Q. Walker and D. L. Ahlberg, *Analyt. Chem.*, 1963, **35**, 2028.

TABLE 2

Thermolysis of 2- and 6-methylazulene in the presence of azomethane

	% Rearrangement	Products (%) N	1-MN	2-MN	1,2-DMN	1,3-DMN	1,4-DMN	2,3-DMN	1,5-DMN	1,6-DMN	1,7-DMN	1,8-DMN	2,6-; 2,7-DMN
2-MA	83·6	0·4	9·8	37·1	23·7	11·9		12·7		1·0	1·3		1·9
6-MA	95·6	0·5	4·7	40·5	1·1	1·6	0·5	0·7	0·5	10·6	16·7	1·0	21·7

The thermolysis product of dimethyl azulene-4,5-dicarboxylate was treated exhaustively with dimethyl sulphate and methanolic sodium hydroxide, and analysed as described above.

TABLE 3

Thermolysis of the methylazulenes

		1-MA	2-MA	4-MA	5-MA	6-MA
% Conversion [a]		87·8	73·8	86·8	97·2	86·7
Products (%) [b]	N	3·9	3·8	12·0	3·2	2·2
	1-MN	56·9	25·1	69·5	45·7	2·7
	2-MN	28·0	58·3	3·6	42·2	88·8
	1,2-DMN	2·9	4·8			
	1,3-DMN	3·2	2·0			
	1,4-DMN	0·5				
	2,3-DMN	0·8	2·3			
	1,5-DMN			5·4	1·3	
	1,6-DMN			4·2	2·5	0·8
	1,7-DMN			3·5	2·7	1·4
	1,8-DMN			1·1	1·6	
	2,6-; 2,7-DMN			0·4	1·4	2·2
	A	3·1	3·2	0·3	0·3	0·6
	1-MA		0·5			
	2-MA	0·6				
	4-MA				0·3	0·07
	5-MA			0·2		1·1
	6-MA				0·7	

[a] Under these standard conditions, azulene conversion was 61·9% to naphthalene only. [b] A blank entry signifies <0·05%.

In a limited search we were unable to find a column which would resolve *N*-methylazulene-4,5-dicarboximide from *N*-methylnaphthalene-1,8-dicarboximide, a possible product. However the latter was stable under the conditions used to thermolyse the former and the problem was at least partially solved by prolonging the thermolysis until it was almost complete. The column used for the analysis reported was a 1 m packed column with 10% Carbowax 20M (polyethylene glycol) stationary phase on 60—80 mesh Diatoport S operating at 195°, injection port temperature 250°, and nitrogen carrier gas flow rate of 50 ml min^{-1}.

RESULTS

Thermolysis of di-t-butyl peroxide (DTBPO) (5 mg) in liquid azulene (50 mg) in an ampoule (*ca.* 2 ml) at 156° for 5 h gave no detectable increase in the naphthalene content (0·04%) of our sample of azulene, but produced all five methylazulene isomers in the following relative amounts: 1, 35·9; 2, 51·1; 4, 7·7; 5, 2·2; 6, 3·2%. Dimethylation was not observed. Thermolysis of DTBPO (5 mg) in a liquid mixture of azulene (50 mg) and naphthalene (50 mg) in an ampoule (*ca.* 2 ml) at 156° for 5 h gave azulene and naphthalene in the ratio 42 : 58 and *ca.* 1·2% of methylation products which consisted of the following: 1-MN, 18·6; 2-MN, 3·1; 1-MA, 23·7; 2-MA, 44·0; 4-MA, 6·5; 5-MA, 1·5; 6-MA, 2·6%.

Thermolyses of DTBPO in azulene vapour at 156° have recently been carried out by Wilshire.[13] DTBPO (1—3 mg) and azulene (5 mg) were heated for 2 h in an ampoule (75 ml). The formation of naphthalene (2—12% of volatile products) was observed in all cases, though the yield did not appear to be a simple function of the DTBPO concentration. In some runs, especially at the higher DTBPO concentrations, formation of methylazulenes was observed, recovery of volatile material was only 60—80%, and a brown residue was formed on the walls of the ampoule. In other runs the recovery of volatile material was high (>90%) and methylazulene formation was not detected (<0·1% of any isomer). Several features of these thermolyses require further study, but the catalysis of rearrangement seems firmly established.

TABLE 4

Thermolysis of the dimethylazulenes

		1,3-DMA	4,5-DMA	4,6-DMA	4,7-DMA	4,8-DMA	5,6-DMA	5,7-DMA
% Conversion		83·7	>99·0	89·2	95·7	82·4	98·5	>99·5
Products (%)	N		0·3	0·1	0·2	0·3	0·1	0·3
	1-MN	2·0	18·4	2·0	3·5	19·0	1·8	1·3
	2-MN	1·6	2·9	12·3	8·8	0·5	7·4	3·7
	1,2-DMN	1·2	47·6	12·9	0·8		46·3	1·2
	1,3-DMN	54·9	5·0	52·3	20·7		3·0	61·6
	1,4-DMN	26·2	0·5	2·9	45·6	26·4		1·8
	2,3-DMN		0·2				30·8	10·7
	1,5-DMN		1·7			11·1		
	1,6-DMN		2·9		0·5	19·4		0·5
	1,7-DMN		4·0	1·0	0·9	13·8	0·3	0·5
	1,8-DMN		1·1			4·1		
	2,6-; 2,7-DMN		0·7	3·3	2·3	0·5	1·0	1·5
	TMNs	11·8	14·7	13·1	16·7	5·1	9·1	16·9
	1-MA	0·7						
	2-MA	0·4						
	1,2-DMA	1·2						

Thermolysis of azulene (10 mg) and azomethane (*ca.* 0·34 mg) in a standard ampoule (100 ml) (as used for the 440° thermolyses) at 310° for 3 h gave the following product

[13] R. W. Alder and C. Wilshire, unpublished results.

composition: N, 24·1; 1-MN, 7·0; 2-MN, 5·4; A, 60·2; 1-MA, 0·9; 2-MA, 2·0% with *ca.* 0·1% each of 4-, 5-, and 6-MA. In a control thermolysis with no azomethane, the naphthalene content of our sample of azulene increased from 0·04 to 0·4%. The results of thermolyses of 2- and 6-methylazulene (10 mg) and azomethane (*ca.* 0·7 mg) at 310° for 3 h are in Table 2. Dimethylazulenes were not determined but the amounts formed were small.

TABLE 5

Rearrangement rates of the methylazulenes

	Individual thermolyses (440°)		Co-thermolysis (440°)	
Compound	$10^5k/s^{-1}$	Relative rate	$10^5k/s^{-1}$	Relative rate
A	13·3	1·0	29·9	1·0
1-MA	29·1	2·2	35·4	1·2
2-MA	18·3	1·4	31·8	1·1
4-MA	27·8	2·1	32·9	1·1
5-MA	49·3	3·7	38·0	1·3
6-MA	27·8	2·1	34·5	1·2

Product compositions from thermolyses of the methylazulenes under the standard conditions (see Experimental section) are in Table 3. Those from the dimethylazulenes are in Table 4. Although temperature control in our thermolyses was only moderate, it is apparent that there are differences (though small ones) in the rates at which different azulenes rearrange. Approximate first-order rate constants for the methylazulenes are in Table 5, along with those calculated from an experiment in which each methylazulene (2 mg) and azulene (2 mg) were thermolysed together for 1 h at 440° in the standard ampoule. The smaller spread of relative rates and the higher rates for the slower reacting compounds in the latter experiment are almost certainly significant.

In order to see if co-thermolysis changed product distributions, 2- and 6-methylazulene (5 mg each) were co-thermolysed under standard conditions. N 4, 1-MN 14·7, 2-MN 72·7, and A 1·9% were obtained compared with mean values calculated from separate thermolyses of 3·0, 13·9, 73·6, and 1·9%, respectively.

In order to examine the effects of variable experimental conditions on product compositions, a number of runs were made with 2-, 4-, and 6-methylazulene. The results are in Tables 6—8. It is apparent that variation of pressure, temperature, and ampoule surface condition and the presence of various additives has very little effect on product composition.

Standard thermolysis of benz[*a*]azulene gave 66·8% conversion with the products consisting of 60·5% phenanthrene and 24·1% anthracene along with two unidentified components, 7·7 and 5·7%, one with *m/e* 180. 9,10-Dihydroanthracene was not present, but the presence of 9,10-dihydrophenanthrene is not disproved. Thermolysis of benz[*f*]azulene was fast (>99·9% conversion) and very clean (>98% phenanthrene). The absence of more than 1% anthracene was checked by u.v. Approximate rate constants for the benzazulenes in separate and co-thermolyses are in Table 9.

Standard thermolysis of dimethyl azulene-4,5-dicarboxylate gave a complex mixture with at least 18 components (in a preliminary communication [10] it was reported that no naphthalenes were obtained; this result was obtained when working at the pressure used by Kallen rather than the lower value employed subsequently). The following naphthalene products were identified (yields are approxi-

TABLE 6

Thermolysis of 2-methylazulene under various conditions

Conditions	% Conversion	N	1-MN	2-MN	1,2-DMN	1,3-DMN	2,3-DMN	A	1-MA
Standard	73·8	3·8	25·1	58·3	4·8	2·0	2·3	3·2	0·5
390°, 24 h	80·0	2·3	28·0	56·8	4·7	2·0	2·3	3·4	0·5
2-MA (2 mg) + A (10 mg)	61·1	?	34·0	62·3	1·8	0·5	0·8	?	0·6
2-MA (2 mg) + 2,6-DMN (10 mg)	40·0	1·9	24·1	57·2	6·6	2·0	2·3	5·3	0·6

TABLE 7

Thermolysis of 4-methylazulene under various conditions

Conditions	% Conversion	N	1-MN	2-MN	1,5-DMN	1,6-DMN	1,7-DMN	1,8-DMN	2,6-; 2,7-DMN	A	5-MA
Standard	86·8	12·0	69·5	3·6	5·4	4·2	3·5	1·1	0·4	0·3	0·2
700 ml ampoule, 440°, 2 h	73·5	7·4	69·8	3·3	6·6	5·0	3·9	1·6	0·8	0·8	0·8
4-MA (2 mg) + A (30 mg)	80·7	?	90·3	9·7							

TABLE 8

Thermolysis of 6-methylazulene under various conditions

Conditions	% Conversion	N	1-MN	2-MN	1,6-DMN	1,7-DMN	2,6-; 2,7-DMN	A	4-MA	5-MA
Standard	86·7	2·2	2·7	88·8	0·8	1·4	2·2	0·6	0·07	1·1
Acid washed ampoule	86·9	2·0	2·8	88·9	0·7	1·4	2·3	0·7		1·2
Silanised ampoule	86·2	2·2	2·8	89·2	0·7	1·5	2·2	0·6		1·1
Silvered ampoule	87·6	1·8	2·3	90·1	0·6	1·1	1·9	0·8	0·09	1·5
Glass wool packed	99·4	2·9	3·1	88·1	1·1	1·7	2·6		0·2	0·3
700 ml ampoule	74·7	2·1	2·7	88·9	0·7	1·5	2·2	0·6		1·1
1 atm. argon	83·2	1·3	2·0	90·8	0·6	1·1	1·9	0·8		1·5
1 atm. benzene	81·2	1·7	1·9	90·9	0·7	1·1	1·8	0·6	0·07	1·3
430°, 2 h	70·2	1·8	1·8	90·3	0·7	1·2	1·9	0·8		1·3

mate): dimethyl naphthalene-1,2-dicarboxylate 42·5; methyl 1-naphthoate 18·5; methyl 2-naphthoate 2·1; methyl 1-methoxy-2-naphthoate 0·6; methyl 2-methoxy-1-naphthoate 1·6; naphthalene 0·2%. Conversion was >99%. Dimethyl naphthalene-1,2-, -1,8-, and -2,3-dicarboxylates were not completely stable under the pyrolysis conditions, but the degree of decomposition was small and similar for each ester.

TABLE 9

Rearrangement rates of the benzazulenes

	Individual thermolyses (440°)		Co-thermolysis (440°)	
	$10^5k/s^{-1}$	Relative rate	$10^5k/s^{-1}$	Relative rate
Azulene	13·3	1·0	36·2	1·0
Benz[*a*]azulene	15·3	1·2	49·4	1·4
Benz[*f*]azulene	>96	>7·2	92·8	2·6

Thermolysis of azulene-4,5-dicarboxylic anhydride under standard conditions gave 94·9% naphthalene-1,2- and 5·1% -1,8-dicarboxylic anhydrides as products (analysed as diesters) at 86·9% conversion. Similar thermolysis of the *N*-methylimide was slow (22% conversion) and gave a product containing *N*-methylnaphthalene-1,2-dicarboximide (>83·5%), <5·0% of the 1,8-isomer (see Experimental section for difficulties in analysis) and *ca.* 2·2% *N*-methylnaphthalene-2,3-dicarboximide (identified by g.l.c. retention time only). Thermolyses of the anhydride and imide were quite clean with no sign of decomposition (*e.g.* decarbonylation) products.

DISCUSSION

Radical Catalysis of Rearrangement.—The most important observation made in the course of this study is that the rearrangement of azulene to naphthalene is promoted when azulene is heated in the gas phase with decomposing DTBPO at 156° and with decomposing azomethane at 310°. Both compounds are known sources of methyl radicals, and there are several indications that these species are responsible for the promotion of rearrangement, although the decomposition of DTBPO, in particular, is complicated, and gives rise to other species which might be active. Thus in experiments with both DTBPO and azomethane, rearrangement is accompanied by methylation. Also the addition of methyl radicals to aromatic hydrocarbons like azulene and naphthalene is likely to be reversible at the temperatures used.[14] A rearrangement scheme in which a methyl radical adds to azulene, the radical adduct, $C_{10}H_8Me^{\bullet}$, somehow rearranges until it possesses the structure of a methyl radical adduct of naphthalene, and finally $Me^{\bullet}$ is lost, is therefore entirely reasonable.

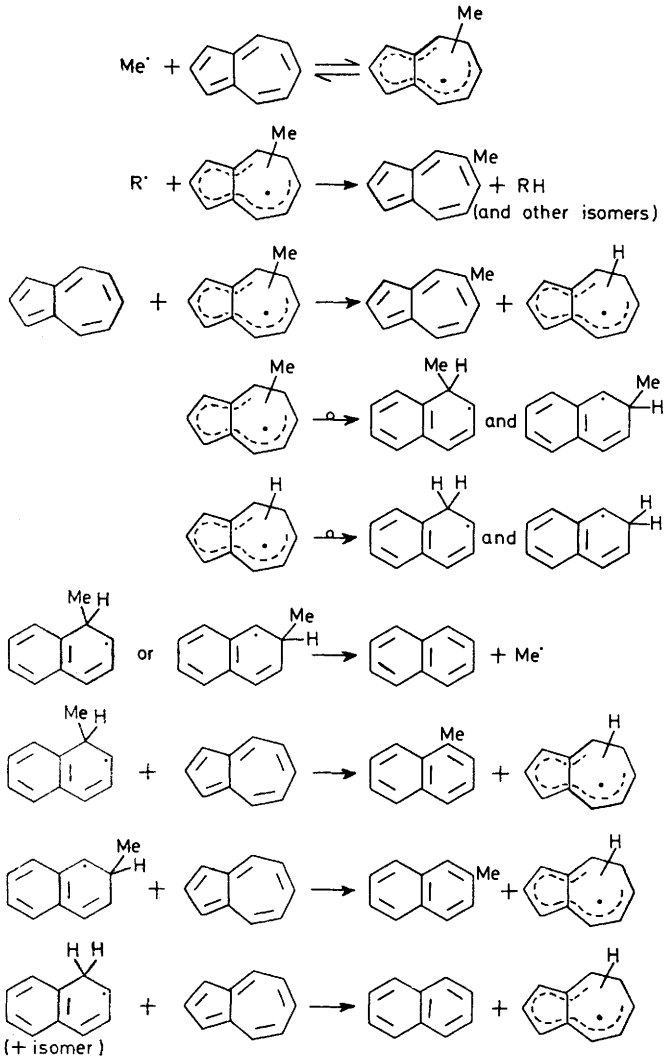
Azomethane decomposition at 310° was also shown to promote the rearrangement of 2- and 6-methylazulene (Table 2). Moreover, the products obtained are qualitatively similar to those obtained from these isomers in direct thermolysis (Table 3). Thus 2-methylazulene gives 1,2-, 1,3-, and 2,3-dimethylnaphthalene in the ratio 2·0 : 1·0 : 1·07 in the azomethane experiment and 2·4 : 1·0 : 1·15 in the 440° thermolysis. Naphthalene is also obtained in the azomethane experiment as well as both 1- and 2-methylnaphthalene (though, perhaps significantly, the ratio of these two is different from the 440° thermolysis). These results strongly suggest that the mechanism of the direct thermolysis is the same as that of the azomethane-promoted reaction, and encourage an attempt to find explanations for the complex product distributions observed in thermolyses of substituted azulenes in terms of rearrangement pathways of radical adducts.

Azulene only rearranges to naphthalene in the presence of decomposing DTBPO when the reaction is done in the gas phase. Decomposition of DTBPO in liquid azulene results in methylation of azulene but no naphthalene or methylnaphthalenes are formed. Methylation of azulene requires a bimolecular hydrogen abstraction and a simple interpretation of the difference between the reactions in the gas and liquid phases is that in the latter situation the radical adduct, $C_{10}H_8Me^{\bullet}$, suffers such rapid bimolecular destruction (by hydrogen abstraction, *etc.*) that it does not live long enough to undergo the unimolecular rearrangement reactions of which it is capable. Even in the gas-phase experiments, hydrogen abstraction must occur, so that the situation is really much more complicated. An elaboration of this simple proposal is shown in Scheme 1, though this is doubtless still too simplified. However there are clearly many questions raised by Scheme 1 which cannot be answered without more work. In particular we cannot say how much naphthalene comes from $C_{10}H_8Me^{\bullet}$ and how much from $C_{10}H_9^{\bullet}$ radicals (or indeed from other $C_{10}H_8R^{\bullet}$ radicals).

Radical Methylation of Azulene.—The methylation of azulene which occurs in both solution and gas-phase experiments calls for some comment. The major isomers formed are 1- and 2-methylazulene and this accords with the observation of Waters and Tilney-Bassett [15] that attack of $PhCH_2^{\bullet}$ gives mainly 1- and 2-benzylazulene. As these authors pointed out, atom localisation energies, calculated by the simple Hückel MO method predict the order of reactivity $4 \geqslant 1 > 5 > 2 > 6$ for attack by radicals at various positions in azulene. Calculations [16] using a more sophisticated π-electron method based on that of Pople give values of atom localisation energies of 2·05 (HMO 2·36), 1·98 (2·24), 2·05 (2·34), and 2·33 for the 2-, 4-, 5-, and 3a-positions of azulene. These figures do not seem to alter the reactivity order suggested by simple Hückel theory, and there is thus some conflict between π-electron theory and experiment, if indeed $CH_3^{\bullet}$ attack is the rate-determining step in the methylation reactions. A factor which might aid attack in the five-membered ring, and which is not considered by π-electron theory, is the relief of σ-bond strain as the attacked carbon goes from sp^2 to sp^3 hybridisation. In an attempt to provide a further basis for comparison, a 1 : 1 mixture of azulene and naphthalene was heated with DTBPO. This

[14] R. A. Jackson, *J.C.S. Chem. Comm.*, 1974, 573.
[15] W. A. Waters and J. F. Tilney-Bassett, *J. Chem. Soc.*, 1959, 3123.
[16] G. L. Caldow, *Mol. Phys.*, 1970, **18**, 383.

experiment however revealed a point of more general significance, namely that the ratio of azulene to naphthalene (42 : 58) in the product had changed by far more than could be accounted for in terms of the methylation which occurred. This is not too surprising,



SCHEME 1

but the fact that methylation is a minor outcome of azulene consumption seems to us to make it risky to ascribe too much significance to the isomer ratios observed. We therefore regard the question of the relative rates of attack of methyl radicals on the various positions in azulene as unresolved at present.

Rates of Thermolysis of Substituted Azulenes.—Our data (Table 5) for the rates of rearrangement of substituted azulenes are only approximate, but it is clear that the variations in rate are small. This suggests that all the azulenes studied rearrange by similar mechanisms. For the monomethylazulenes and also for the two benzazulenes studied, these small differences are further reduced in co-thermolyses. This probably means that variation in the ease of production of initiating radicals accounts for a major fraction of these rate variations. The rate of rearrangement of 6-methylazulene was increased by increasing the surface area : volume ratio of the ampoule and decreased by decreasing the total pressure in the ampoule (Table 8). These changes are in accord with the observations of Kallen and Heilbronner [2] on azulene itself and again probably mainly reflect changes in initiation rate. Significantly, there is almost no effect on product composition.

Thermolysis Product Compositions.—The product compositions from thermolyses of the methyl- and dimethylazulenes are complex and are clearly incompatible with a simple unimolecular rearrangement pathway. However, this complexity means that these product distributions provide a wealth of mechanistic information and a number of important trends and features can be discerned by inspection of Tables 3 and 4.

(i) Rearrangement to isomeric azulenes is negligible (<1%) under the reaction conditions. Since the rates of rearrangement of isomeric azulenes are very similar, we can conclude that only a few percent, at most, of naphthalene products can arise *via* the formation and subsequent rearrangement of isomeric azulenes. In addition to this we have checked that the naphthalenes formed are stable to the reaction conditions. Thus, for example, the 25% of 1-methylnaphthalene which is produced from 2-methylazulene cannot arise from isomerisation of 2-methylazulene to the 1-isomer and subsequent rearrangement of this.

(ii) Demethylation (*e.g.* formation of naphthalene from methylazulenes) is observed in all cases (2—20% of products). With azulenes substituted in the five-membered ring (1- and 2-methylazulene and 1,3-dimethylazulene) a substantial portion, if not all, of the demethylated naphthalene products may arise from demethylated azulenes. Azulenes with substituents in the seven-membered ring appear to lead to demethylated naphthalenes directly, since demethylated azulenes are formed in much smaller amounts in these cases. Demethylation is most prominent when 4-methyl substituents are present. A further point to notice is that decreasing the pressure seven-fold (and other changes of thermolysis conditions) has only a small effect on the amount of naphthalene obtained from 4- and 6-methylazulene (Tables 7 and 8). It is therefore likely that demethylation in these cases shares the same basic mechanism as rearrangement to isomeric naphthalenes.

(iii) Methylation also occurs in every case examined, and to approximately the same extent as demethylation. With methylazulenes, where analysis of the methylation products (dimethylnaphthalenes) was possible, the methylation shows a remarkable and interesting specificity. 1- and 2-Methylazulenes only give dimethylnaphthalenes which have both methyl groups in the same ring, whereas 4-, 5-, and 6-methylazulenes only give those dimethylnaphthalenes with one methyl group in each ring. 4-Methylazulene, for example, gives 1,5-, 1,6-, 1,7-, and even 1,8-dimethylnaphthalene but little of the 2,6- and 2,7-isomers. This could perhaps arise if

the original 4-methyl substituent stayed put, but an introduced methyl was free to find its way to any position in the naphthalene ring which was originally the azulene five-membered ring.

(iv) In all cases, the major products are naphthalenes isomeric with the starting azulene. In most cases the major isomeric product is the one expected on the basis of minimal structural change. However, in several cases, products are formed in major amounts which do not correspond to the principle of minimal structural change. Thus (*a*) from 2-methylazulene, half as much 1- as 2-methylnaphthalene is formed. It remains to be seen whether the 1 : 2 ratio of these products is significant, but as discussed under (i) there seems to be no trivial explanation in terms of azulene–azulene rearrangements. (*b*) 1,3-Dimethylazulene gives 1,3- and 1,4-dimethylnaphthalenes in a 2 : 1 ratio. Only 1·2% of 1,2-isomer is formed (this might arise from a rearranged azulene; 1·2% of an unknown, probably dimethylazulene is observed) and no 2,3-dimethylnaphthalene is seen. This virtual absence of the 1,2- and 2,3-isomers seems to rule out any process which exchanges C-1 and -2 of azulene (or their substituents) during the course of the azulene–naphthalene rearrangement. Exchanges of C-1 and -2 substituents have been observed in azulene–azulene rearrangements promoted by heterogeneous catalysis.[4,5] If exchange of C-1 and -2 does not occur in other cases, the formation of 1-methylnaphthalene from 2-methylazulene becomes all the more remarkable. (*c*) With 4,6-, 4,7-, 4,8-, and 5,7-dimethylazulenes, a substantial quantity of that dimethylnaphthalene is produced which possesses one less carbon atom between the substituents (*i.e.* the 1,2-, 1,3-, 1,4-, and 2,3-isomers respectively). This suggests a possible mechanism in which an intervening carbon is removed from between the substituted carbons in the course of the rearrangement. In accord with this idea, the percentage of this product formed increases with the number of carbons which intervene. (*d*) All the azulenes with two methyl groups in the seven-membered ring give some dimethylnaphthalenes with one methyl group in each ring. In 4,8-dimethylnaphthalene, which gives the greatest amounts of these products, the methyl group which is apparently transferred from one ring to the other can ultimately end up in all possible positions of the latter (expanded) ring. This recalls the similar situation observed for the methylation products of 4-methylazulene. Taken with the results in (iv)(*c*) there is a strong hint that rearrangement involves the migration of one carbon (with its substituents) from this originally seven-membered ring into the former five-membered ring.

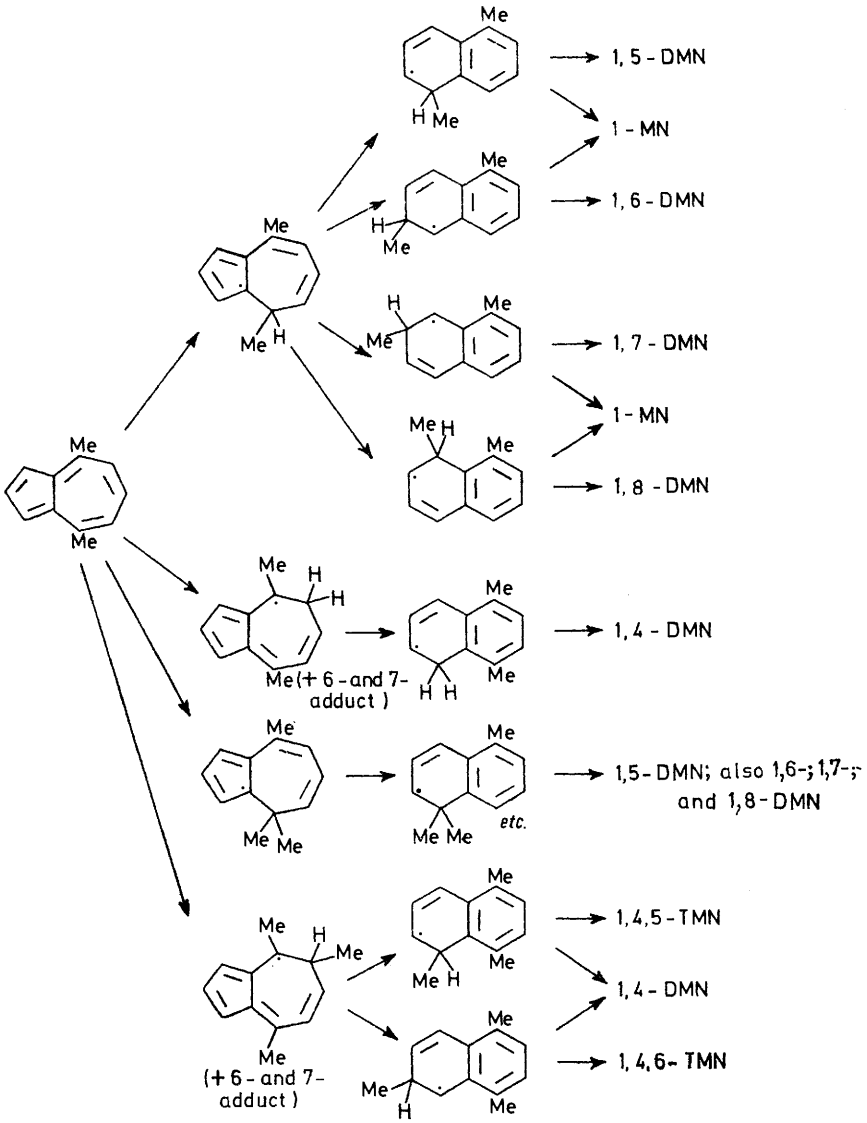
Rearrangement Mechanisms.—The principle suggestion to emerge from an examination of thermolysis product compositions is that one ring carbon from amongst C-4—C-8 migrates with its substituent(s) into the former five-membered ring. This must be treated as a postulate until direct evidence can be obtained (^{13}C studies are in progress). However this postulate, taken with a few others, provides an economical explanation of the main features of the product distributions described above. We assume, for the present, that all the other ring carbons maintain their relative positions. This allows the [4.4.0]decane skeleton to be created. We next suppose that the migrating carbon is the one which undergoes attack by H· or Me· to form the radical adduct, and that the added group and the original substituent remain attached to the migrating carbon throughout the rearrangement. We also suppose this carbon may find its way to any position in the former five-membered ring and that finally either H· or Me· is lost from the migrating carbon to give the naphthalene product.

The results of these postulates are best demonstrated with an example, 4,8-dimethylazulene (Scheme 2). It can be seen that Scheme 2 explains the formation of all the products observed in >1% yield, and does not predict the formation of any products which are not in fact observed. Moreover the amounts of different products formed seem entirely reasonable in terms of Scheme 2. Similar schemes based on the postulates set out above account well for the product distributions from the other seven-membered ring substituted azulenes in Tables 3 and 4, with one or two minor exceptions. The largest exception is the 5% of 1,3-dimethylnaphthalene formed from 4,5-dimethylazulene. A possible source of this is 4,6-dimethylazulene formed by rearrangement of the 4,5-isomer, but thermolysis of the 4,5-isomer to lower conversions did not reveal this compound. Despite these exceptions, the agreement of the predictions based on the rules set out above with experiment in the case of the seven-membered ring substituted azulenes must be regarded as impressive. Furthermore it is quite easy to devise reasonable molecular mechanisms to explain the rearrangements observed. As an example, Scheme 3 explains the formation of 1,6-dimethylnaphthalene from 4,8-dimethylazulene in terms of a sequence of rearrangements which are closely analogous to the well-known homoallyl–cyclopropylcarbinyl radical rearrangement.[17] Similar mechanisms can explain the other products observed.

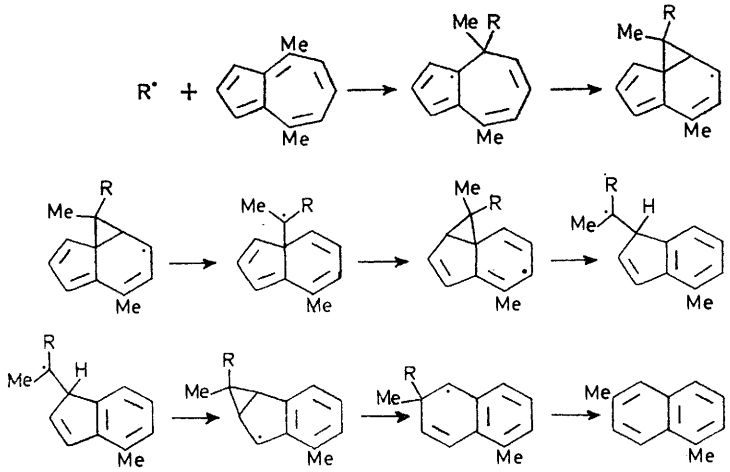
The results of thermolyses of benz-[*a*]- and -[*f*] azulenes, of dimethyl azulene-4,5-dicarboxylate and of its derived anhydride and imide are also in general consistent with the rules and mechanisms proposed above. The exclusive formation of phenanthrene in the thermolysis of benz[*f*]azulene is reasonably explained in terms of a strong preference for radical attack at position 4. The 2·2% of *N*-methylnaphthalene-2,3-dicarboximide is not accounted for, but might result from an azulene–azulene rearrangement.

Unfortunately, the limited results available for the five-membered ring methylated azulenes do not entirely support the description of the rearrangement in terms

[17] A. L. J. Beckwith in ' Essays in Free Radical Chemistry,' ed. R. O. C. Norman, Chem. Soc. Special Publ., No. 24, 1970; L. K. Montgomery, J. W. Matt, and J. R. Webster, *J. Amer. Chem. Soc.*, 1967, **89**, 923; E. C. Friedrich and R. L. Holmstead, *J. Org. Chem.*, 1971, **36**, 971.

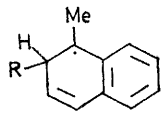


SCHEME 2



SCHEME 3

of Schemes 2 and 3. A majority of the products observed can still be accounted for, but there are several problems. In particular the 25% 1-methylnaphthalene formed from 2-methylazulene is unexpected. Quite simply, in terms of the proposals made above, there is no necessity for this substituent migration to occur. The 4·8% of 1,2-dimethylnaphthalene from 2-methylazulene is also not explicable. Although this is a fairly minor product in the direct thermolysis, it is the major methylation product, and in the azomethane-promoted thermolysis it constituted 23·7% of the products. It



(1)

seems possible that the formation of these two products, 1-methylnaphthalene and 1,2-dimethylnaphthalene, are related, since both could arise from radicals like (1; R = H or Me). The amounts of (1) with R = H and with R = Me might be expected to vary between direct and azomethane-promoted thermolysis in a way which could explain the changes in product ratios observed. However, if in (1) CHR is the intact group which has migrated from the former seven-membered ring, as seems most reasonable, then one is led to expect a related intermediate in the 1,3-dimethylazulene thermolysis which on loss of R would give 1,2-dimethylnaphthalene. But this in fact is a very minor product of thermolysis of this compound. It is possible that (1) only arises in substantial amounts when the radical centre is tertiary (*i.e.* C-2 has a methyl group). However Wilshire has recently observed[13] that thermolysis of 2-deuterioazulene under standard conditions gives a naphthalene product whose 100 MHz ^{1}H n.m.r. spectrum indicates that it is a mixture of 1- and 2-dueterionaphthalene.

We have not yet been able to devise a mechanism for the azulene–naphthalene rearrangement which fits all the results known to date. The type of mechanism pictured in Schemes 1—3 seems to have much in its favour. If we seek to modify it to encompass the results which it does not explain, there seem to be two places where this might reasonably be done. The *first* is at the initial step of radical attack on the azulene. Schemes 2 and 3 suppose that only attack in the seven-membered ring is productive of rearrangement, yet the indications are that radicals attack azulene most easily in the five-membered ring. In particular the troublesome 2-position is apparently the one most susceptible to radical attack. Perhaps when the five-membered ring is substituted other processes occur, yet the rates of rearrangement of 1-methyl-, 2-methyl-, and 1,3-dimethylazulene are unexceptional.

The other and, in our opinion, more promising, place where one may seek to modify Schemes 2 and 3 is in the later stages of the rearrangement where the migrating group is entering the five-membered ring. Thus a process whereby C-2 and the migrating carbon change places is attractive, but we are unable to propose a satisfying molecular explanation of how and why this might occur. It is as well to end on a cautionary note. The rearrangements utilised in Scheme 3 have been likened to homoallyl–cyclopropylcarbinyl rearrangements. This analogy should not disguise the fact that several of the steps are really electrocyclic reactions of radicals. It has been pointed out that all reactions of this type are ' forbidden ' by state symmetry,[18,19] but nevertheless occur *via* an ' avoided crossing.' The energetics of such reactions cannot be predicted in any simple way.[19]

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[4/2190 *Received*, 24*th October*, 1974]

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