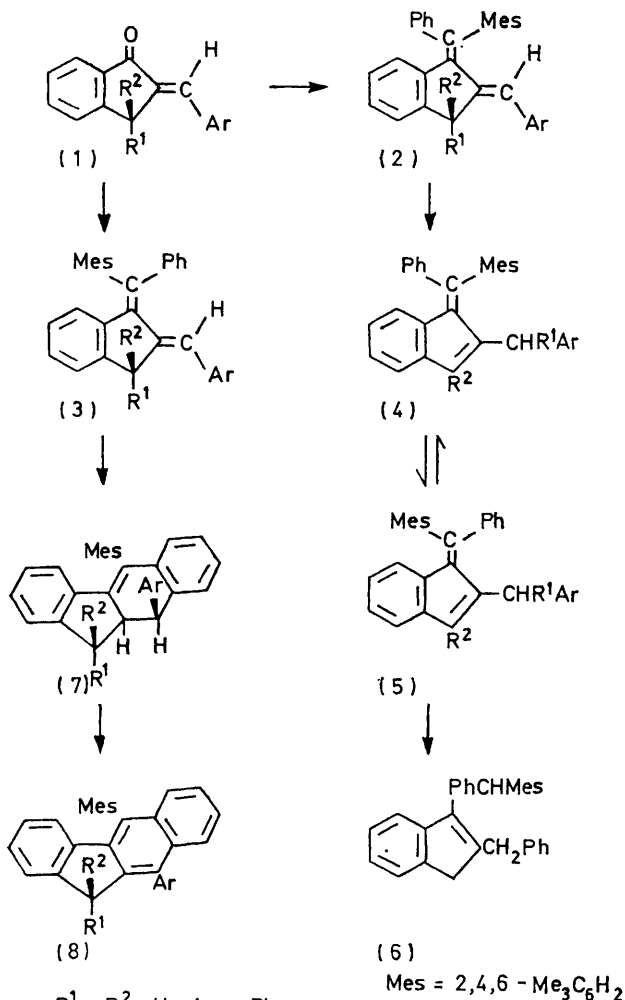


Overcrowded Molecules. Part XI.^{1,2} A Doubly 'Forbidden' Symmetry-allowed Pericyclic Reaction: the Thermal Rearrangement of (*E*)-2-Benzylidene-(*Z*)-1-mesityl(phenyl)methyleneindane into (*Z*)-2-Benzyl-1-mesityl(phenyl)methyleneindene

By John S. Hastings, Harry G. Heller,* and Howard Tucker, Edward Davies Chemical Laboratories, University College of Wales, Aberystwyth SY23 1NE
(in part) Keith Smith, Chemistry Department, University College of Swansea, Swansea SA2 8PP

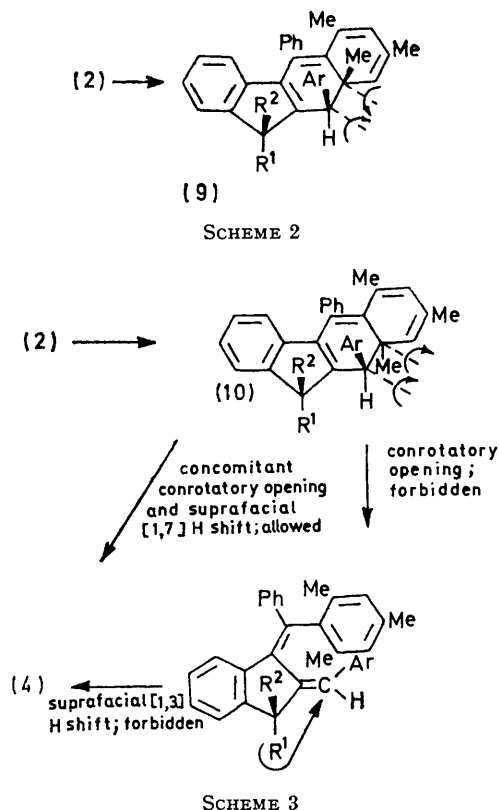
(*E*)-2-Benzylidene-(*Z*)-1-mesityl(phenyl)methyleneindane cyclises by a disrotatory mode at 180 °C to give *cis*-9a,10-dihydro-5,10-diphenyl-6,8,9a-trimethyl-11*H*-benzo[*b*]fluorene, which, at this temperature, undergoes two 'forbidden' processes in concert, namely conrotatory ring opening and a suprafacial [1,7] hydrogen shift, to yield (*Z*)-2-benzyl-1-mesityl(phenyl)methyleneindene.

RING opening reactions of cyclohexadiene systems proceeding by a conrotatory mode and suprafacial [1,3]



hydrogen shifts are symmetry-forbidden³ thermal processes involving anti-aromatic transition states⁴ and are

not known. When it is possible for two 'forbidden' processes to proceed together, the pericyclic reaction can occur with conservation of orbital symmetry, through an aromatic transition state, in accord with the selection rules. We report here the first examples of this type of reaction.



Mesityl(phenyl)keten reacts with (*E*)-2-benzylideneindan-1-one (1a) at 140 °C to give the dimethyleneindanes (2a) and (3a) and, from their thermal rearrangement, the benzofulvenes (4a) and (5a). The dimethyleneindane-benzofulvene rearrangement (2a) → (4a) is the first clear example of a symmetry-allowed

¹ Part X, H. G. Heller and M. Szewczyk, *J.C.S. Perkin I*, 1974, 1487.

² J. S. Hastings, H. G. Heller, H. Tucker, and K. Smith, *J.C.S. Chem. Comm.*, 1974, 348.

³ R. B. Woodward and R. Hoffmann, *Accounts Chem. Res.*, 1968, **1**, 17.

⁴ H. E. Zimmerman, *Accounts Chem. Res.*, 1971, **4**, 272.

pericyclic reaction involving two 'forbidden' processes, namely thermal conrotatory ring opening of a six-electron system and a concomitant suprafacial [1,7] hydrogen shift.

The structures of the dienes (2a) and (3a) follow from the similarity of their u.v. and n.m.r. spectra to those of (*E*)-2-benzylidene-1-diphenylmethyleneindane^{5,6} and from their photodehydrocyclisation in hexane to 5-mesityl-10-phenyl-11*H*-benzo[*b*]fluorene (8a). The stereochemistry of the diene (2a) was assigned from the observation that, on heating at 180 °C, it rearranges to the benzofulvene (4a) rather than undergo cyclisation on to the phenyl group, followed by a [1,5] hydrogen shift, to give the *cis*-10,10a-dihydrobenzo[*b*]fluorene (7a).

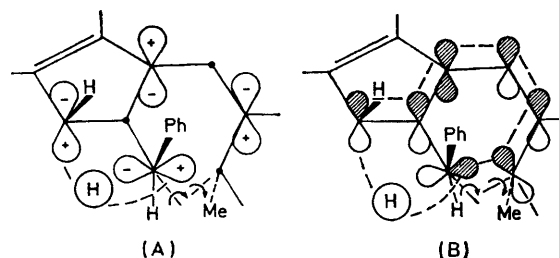
The synthesis of the diene (2a) was undertaken in the expectation that, on irradiation at 366 nm, it would undergo electrocyclic conrotatory ring closure to give the more deeply coloured intermediate (9a), which would be thermally stable because of steric interactions which must occur in the allowed disrotatory ring opening and the unlikelihood of a methyl shift at room temperature (*cf.*⁷ the stability of 1,8a-dihydro-1,1,5,7,8a-pentamethylnaphthalene-2,3-dicarboxylic anhydride at 160 °C). The intermediate (9a) could not be detected and it is believed that photochemical isomerisation of the diene (2a) to the diene (3a) is the preferred process, with subsequent conrotatory ring closure onto the phenyl group, followed by dehydrogenation.

The structures of the benzofulvenes (4a) and (5a) were assigned from the close similarity of their u.v. and n.m.r. spectra to that of 2-benzyl-1-diphenylmethyleneindene⁶ and from the fact that they undergo no thermal or photochemical rearrangements other than interconversion. On reduction with aluminium amalgam, they yield 2-benzyl-3-mesityl(phenyl)methylindene (6), whose u.v. and n.m.r. spectra resemble those of 2-benzyl-3-diphenylmethylindene.⁶ The stereochemistry of the benzofulvenes is assigned on the basis that the mesityl group exerts a greater shielding effect on the methylene protons in the *Z*-isomer (4a) (τ 6.96) than does the phenyl group in the *E*-isomer (5a) (τ 6.48).

Mesityl(phenyl)keten did not react with (*E*)-2-benzylidene-3-methylindan-1-one (1b) at 140 °C. At 180 °C, *r*-10,*c*-10a-dihydro-5-mesityl-*c*-11-methyl-10-phenyl-11*H*-benzo[*b*]fluorene (7b) was obtained, formed by ring closure of the diene (3b) by the sterically less hindered disrotatory mode on to the phenyl group, followed by a [1,5] hydrogen shift (*cf.*⁵ the thermal rearrangement of 2-benzylidene-1-diphenylmethylene-3-methylindane). No benzofulvene was detected, nor would the benzofulvene (4b) be expected to be formed in a concerted process from the intermediate (10b), since only the 11-hydrogen atom *anti* to the 10-phenyl substituent can migrate if orbital symmetry is to be conserved. The absence of benzofulvene derivatives in this and the previously reported^{5,8-10} dimethyleneindane

rearrangements precludes an acid- or a radical-catalysed [1,3] hydrogen shift in the diene-benzofulvene rearrangement (2a) \rightarrow (4a).

The thermal rearrangement of the diene (2a) at 180 °C to give the benzofulvene (4a) can only be explained satisfactorily by two consecutive concerted reactions: (i) disrotatory ring closure to the dihydrobenzofluorene intermediate (10a), followed by (ii) opening of the newly formed σ -bond by the conrotatory mode, not prevented by steric constraints, with a concomitant suprafacial [1,7] shift of the 11-hydrogen atom *anti* to the 10-phenyl group and retention of configuration at the migration terminus, as shown below. This [$\pi 4_s + \sigma 2_s + \sigma 2_s$] process occurs with conservation of orbital symmetry [Figure (A)] and



MO presentation showing conservation of orbital symmetry (A) and Möbius transition state (B) for thermal conrotatory ring opening and a concomitant [1,7] H shift in (10a)

involves a Möbius transition state (B). The rearrangement (2a) \rightarrow (4a) can be broken down into two 'forbidden' processes, a conrotatory electrocyclic ring opening in a six-electron system, and a suprafacial [1,3] sigmatropic change of order of hydrogen.

In order to establish that hydrogen migration occurs exclusively from the methylene group, 3-deuterioindanone derivatives were studied. In view of the practical difficulties experienced in separating the products from the keten-ketone reactions, (*E*)-*p*-methoxybenzylideneindan-1-one (1c) and its deuterio-derivatives (1d and e) were used, in the expectation that the susceptibility of the carbonyl oxygen atom of these ketones to electrophilic attack by mesityl(phenyl)keten would be enhanced by the electronic effect of the *p*-methoxy-substituent, and that the sharp n.m.r. absorption of the *p*-methoxy-group would provide a convenient probe for establishing product composition. The ketone (1c) with mesityl(phenyl)keten at 140 °C gave the (*Z*)-benzofulvene (4c), which on heating at 180 °C equilibrated to a 1 : 1 mixture of *Z*- and *E*-isomers, (4c) and (5c).

At 140 °C, the ketone (1d) and mesityl(phenyl)keten gave a 1 : 1 mixture of (*Z*)- and (*E*)-benzofulvenes (4d) and (5d). On repeating the reaction at 180 °C, the only products isolated were the benzofluorene (8d) and its dihydro-derivative (7d). Apparently at the higher

⁵ H. G. Heller, D. Auld, and K. Salisbury, *J. Chem. Soc. (C)*, 1967, 1084.

⁶ H. G. Heller and K. Salisbury, *J. Chem. Soc. (C)*, 1970, 873.

¹⁰ H. G. Heller and K. Salisbury, *J. Chem. Soc. (C)*, 1970, 1997.

⁵ H. G. Heller and K. Salisbury, *J. Chem. Soc. (C)*, 1970, 399.

⁶ N. Campbell, P. S. Davison, and H. G. Heller, *J. Chem. Soc.*, 1963, 993.

⁷ H. G. Heller and R. M. Megit, *J.C.S. Perkin I*, 1974, 923.

temperature isomerisation of the diene (2d) to the diene (3d) followed by electrocyclic ring closure on to the phenyl group occurs faster than deuterium migration in the diene (2d) to give the benzofulvene (4d).

Interaction of mesityl(phenyl)keten and the ketone (1e) at 140 °C gave a 5:1 mixture of (*Z*)- and (*E*)-benzofulvenes (4e and f) and (5e and f). The *Z*- and *E*-isomers were separated by fractional crystallisation. A *ca.* 1:4 ratio of intensities of olefinic and methylene absorptions (at τ 3.75 and 7.00, and 3.83 and 6.51, respectively) indicated that 60% migration of hydrogen and 40% migration of deuterium from the methylene group had taken place in the rearrangement (2e) \rightarrow (4e) and (4f), proving the exclusive involvement of the methylene group in the rearrangement.

EXPERIMENTAL

U.v. spectra were measured for solutions in cyclohexane with a Unicam SP 1800A spectrometer; n.m.r. spectra were obtained for solutions in carbon tetrachloride with a Perkin-Elmer R12 (60 MHz) spectrometer (tetramethylsilane as internal standard). Product distributions were determined by measuring the area under characteristic peaks of spectra of crude products after removal of solvent. Solvents were dried and distilled before use. Petroleum refers to the fraction of b.p. 60–80°. For photoreactions, an assembly of four 125 W mercury discharge lamps (type MBW/U, A.E.I. Lamp and Lighting Co., Leicester) with Wood's glass filters was used. Products were separated by column chromatography on alumina (Spence type H) with benzene or benzene-petroleum as eluant.

Reaction of Mesityl(phenyl)keten with the Benzylidene Ketone (1a).—An intimate mixture of mesityl(phenyl)keten¹¹ (5.3 g) and ketone (1a) (5.0 g) was heated (4 h) at 140 °C. About half the resulting melt was removed and triturated with petroleum, and the resulting solid (2.95 g) was chromatographed. The first yellow band gave a mixture of *E,E*- and *E,Z*-dienes (0.35 g), separated by fractional crystallisation from benzene-petroleum (3:1). (*E*)-2-Benzylidene-(*Z*)-1-mesityl(phenyl)methyleneindane (2a) (0.21 g) separated as yellow crystals with an intense blue-green fluorescence, m.p. 199–204° (Found: C, 89.3; H, 6.6. C₃₂H₂₈ requires C, 93.2; H, 6.8%); λ_{\max} 260 and 355 nm (log ϵ 4.38 and 4.17); τ 2.46–3.25 (16H, complex m, ArH), 3.93 (1H, t, *J* 2 Hz, :CH·), 6.10 (2H, d, *J* 2 Hz, CH₂), and 7.73, 7.76, and 7.80 (9H, s, *o*- and *p*-Me). A second crop of orange crystals with a green fluorescence (0.10 g), m.p. 180–181°, was the *E,E*-isomer (3a) (Found: C, 93.0; H, 7.0%); λ_{\max} 260 and 355 nm (log ϵ 4.54 and 4.32); τ 2.61–3.30 (16H, complex m, ArH), 4.05 (1H, t, *J* 2 Hz, :CH·), 6.17 (2H, d, *J* 2 Hz, CH₂), 7.76 (3H, s, *p*-Me), and 7.79 (6H, s, *o*-Me) [*cf.*⁶ (*E*)-2-benzylidene-1-diphenylmethyleneindane]. The second band from chromatography gave unchanged ketone (1a) (2.51 g).

After being heated for a further 10 h at 140 °C, the second half of the reaction mixture was chromatographed. The first yellow band gave a 1:1 mixture of the benzofulvenes (4a) and (5a). Nine fractional crystallisations from benzene-petroleum (1:3) gave pure (*Z*)-2-benzyl-1-mesityl(phenyl)methyleneindene (4a), m.p. 141–142° (Found: C, 93.1; H, 6.7%); λ_{\max} 240, 278, and 342 nm (log ϵ 4.38, 4.07, and 4.04); τ 2.40–3.36 (16H, complex m, ArH), 3.80 (1H, t, *J* 1.8 Hz, :CH·), 6.96 (2H, d, *J* 1.8 Hz, CH₂), 7.74

(3H, s, *p*-Me), and 7.95 (6H, s, *o*-Me). Repeated crystallisation of the combined residues from acetic acid-ethanol gave the *E*-isomer (5a), yellow needles, m.p. 139–140° (Found: C, 93.15; H, 6.85%); λ_{\max} 268, 338, and 344 nm (log ϵ 4.35, 4.22, and 4.22); τ 2.70–3.40 (15H, complex m, ArH), 3.45br (1H, s, :CH·), 3.96 (1H, d, *J* 8 Hz, 7-H shielded by mesityl group), 6.48br (2H, s, CH₂), 7.74 (3H, s, *p*-Me), and 7.95 and 8.08 (6H, s, *o*-Me) (*cf.*⁵ 2-benzyl-1-diphenylmethyleneindene).

When the ketone (1a) (3.2 g) and mesityl(phenyl)keten (3 g) were heated (48 h) at 140 °C, only a 1:1 mixture of (*E*)- and (*Z*)-benzofulvenes (4a) and (5a) (3.43 g) was obtained; these were purified by chromatography and separated as described above.

2-Benzyl-3-mesityl(phenyl)methylindene (6).—Reduction of a 1:1 mixture of (*E*)- and (*Z*)-2-benzyl-1-mesityl(phenyl)methyleneindene (0.3 g) (4a) and (5a) with aluminium amalgam in moist ether (24 h) gave the indene (6) (0.11 g), m.p. 142–143° (from ethanol) (Found: C, 92.5; H, 7.35. C₃₂H₃₀ requires C, 92.75; H, 7.25%); λ_{\max} 265 (log ϵ 4.20); τ 2.6–3.3 (16H, complex m, aromatic), 4.00br (1H, s, methine), 6.58 (2H, s, CH₂), 6.70br (2H, s, CH₂), 7.62 (3H, s, *p*-Me), and 7.80 (6H, s, *o*-Me) [*cf.*⁵ 2-benzyl-3-diphenylmethylindene, λ_{\max} 261 (log ϵ 4.29); τ 2.6–3.3 (19H, complex m, aromatic), 4.28br (1H, s, methine), 6.32 (2H, s, CH₂), and 6.68br (2H, s, CH₂)].

Thermal Rearrangements of the Diene (2a) and the Benzofulvene (4a).—The diene (2a) (60 mg) in *o*-dichlorobenzene (3 ml) was heated (30 h) at 180 °C. Solvent was removed and the residue chromatographed. The first band with a blue fluorescence gave 5-mesityl-10-phenyl-11H-benzo[*b*]fluorene (2 mg) (8a), identified by its characteristic u.v. spectrum { λ_{\max} 270, 311, and 324 nm (log ϵ 4.59, 4.14, and 4.13); *cf.*⁵ 5,10-diphenyl-11H-benzo[*b*]fluorene, λ_{\max} 270, 310, and 323 nm (log ϵ 4.82, 4.25, and 4.28)}. The second band gave a 4:1 mixture of (*Z*)- and (*E*)-benzofulvenes (4a) and (5a) (55 mg).

The (*Z*)-benzofulvene (4a) (500 mg) was boiled (9 h) in *o*-dichlorobenzene. Thermal equilibration occurred and a mixture of (*Z*)- and (*E*)-benzofulvenes (4a) and (5a) was obtained.

Photochemical Reactions of the Dienes (2a) and (3a) and the Benzofulvenes (4a) and (5a).—When *ca.* 10⁻⁵M-solutions of the dienes (2a) and (3a) in hexane were irradiated, the dienes were quantitatively oxidised to the mesitylphenylbenzofluorene (8a) within 1 h, whereas the benzofulvenes (4a) and (5a) under similar conditions showed no change in their u.v. spectra on prolonged irradiation (3 days).

Interaction of Mesitylphenylketen and (E)-2-Benzylidene-3-methylindane-1-one (1b).—Mesitylphenylketen (7.1 g) and (*E*)-2-benzylidene-3-methylindane-1-one (1b) (4.7 g) did not react on heating at 140 °C. The mixture was heated (15 h) at 180 °C under nitrogen and the product was chromatographed (elution with petroleum). The first band gave *r*-10,*c*-10a-dihydro-5-mesityl-*c*-11-methyl-10-phenyl-11H-benzo[*b*]fluorene (7b) (3.6 g), m.p. 200–201° (from acetic acid) (Found: C, 92.5; H, 7.15. C₃₃H₂₈ requires C, 92.9; H, 7.1%), λ_{\max} 244, 313, 330, and 347 nm (log ϵ 4.28, 4.26, 4.42, and 4.31), τ 2.4–3.5 (15H, complex m, aromatic), 3.75 (1H, d, *J* 7 Hz, shielded 4-H), 5.4 (1H, d, *J*_{*cis*-10,10a} 8 Hz, 10-H), 6.58 (1H, t, *J*_{*cis*-10,10a} 8, *J*_{10,11} 8 Hz, 10a-H), 7.0 (1H, quintet, *J*_{10,11} 8, *J*_{11,Me} 8 Hz, 11-H), 7.55, 7.85, and 7.93 (9H, singlets, Me protons of mesityl), and 8.45 (3H, d,

¹¹ R. C. Fuson, L. J. Armstrong, J. W. Kreisley, and W. J. Schenck, jun., *J. Amer. Chem. Soc.*, 1944, **66**, 1464.

$J_{11,Me}$ 8 Hz, 11-Me) (*cf.*⁵ *r*-10,*c*-10a-dihydro-5,10-diphenyl-*c*-11-methyl-11*H*-benzo[*b*]fluorene). Four deep red bands from the column gave red intractable oils. The yellow benzofulvenes could not be detected in this reaction, which was repeated several times with heating for different periods at temperatures ranging from 140 to 180°.*

(*E*)-2-*p*-Methoxybenzylideneindan-1-one (1c) and its 3-Deuterio- and 3,3-Dideuterio-derivatives.—Methyl cinnamate or methyl 3-phenylpropynoate (10 g) in ethyl acetate (20 ml) was shaken with deuterium at atmospheric pressure over 10% palladium-charcoal (1 g). The fully deuteriated ester was hydrolysed with ethanolic 10% w/v potassium hydroxide (25 ml) and the solution was acidified with hydrochloric acid. The deuteriated 3-phenylpropanoic acid (8 g) was treated with thionyl chloride (6 ml) and the resulting acid chloride, b.p. 62–64° at 0.1 mmHg (5 g), was dissolved in petroleum (25 ml) and heated (1 h) in the presence of anhydrous aluminium chloride (7 g) to give the deuteriated indan-1-one (3.8 g, 93%). A solution of the ketone (1.7 g) and *p*-methoxybenzaldehyde (1.7 g) in ethanol (10 ml) was treated with ethanolic 10% w/v potassium hydroxide (0.5 ml). The resulting *p*-methoxybenzylidene derivative¹² was crystallised from ethanol; m.p. 130–140° (3.3 g, 86% yield).

Reaction of Mesityl(phenyl)keten with the *p*-Methoxybenzylidene Ketone (1c) and its Deuterio-derivatives (1d and e).—An intimate mixture of mesityl(phenyl)keten (4.7 g) and the ketone (5.0 g) (1c) was heated (50 h) at 140 °C. Work-up as before gave (*Z*)-1-mesityl(phenyl)methylene-2-*p*-methoxybenzylidene (4c) (2 g), m.p. 178–179° (from toluene-petroleum, 1 : 3); τ 2.70–3.45 (15H, complex m, ArH), 3.75 (1H, *J* 2 Hz, :CH·), 6.23 (3H, s, OMe), 7.00 (2H, d, *J* 2 Hz, CH₂), 7.70 (3H, s, *p*-Me), and 7.93 (6H, s, *o*-Me). No other hydrocarbons were detected. On heating in *o*-dichlorobenzene at 180 °C, a 1 : 1 mixture of (*Z*)- and (*E*)-benzofulvenes (4c) and (5c) was obtained.

When mesityl(phenyl)keten (2.4 g) and the ketone (1d) (2.6 g) were heated (50 h) at 140 °C, a low yield of a 1 : 1 mixture of (*Z*)- and (*E*)-benzofulvenes (4d) and (5d) (60 mg) was obtained. Unchanged ketone (1d) (1.8 g) was recovered. When the reaction was repeated at 180 °C, the only products isolated were 11,11-dideuterio-5-mesityl-10-*p*-methoxyphenyl-11*H*-benzo[*b*]fluorene (8d), its *cis*-10,10a-dihydro-derivative (7d), and unchanged ketone (1d).

Mesityl(phenyl)keten (0.55 g) and the ketone (1e) (0.58 g) were heated (20 h) at 140 °C. The product was dissolved in benzene and chromatographed. The yellow band gave a 5 : 1 mixture of (*Z*)- and (*E*)-benzofulvenes (4e and f) and (5e and f) (0.72 g), from which the *Z*-isomer (4e and f) (0.60 g), m.p. 178–179°, was obtained by crystallisation from toluene-petroleum. Its n.m.r. spectrum showed absorptions at τ 3.75 and 7.00 in the ratio 1 : 4, indicating that a 40% migration of deuterium had taken place.

The mother liquors were evaporated to dryness and the residue was crystallised from ethanol, giving the *E*-isomer (5e and f), m.p. 159–160°; τ 2.60–3.35 (14H, complex m, ArH), 3.83 (1H, t, *J* 2 Hz, :CH·), 3.95 (1H, d, *J* 8 Hz, 7-H shielded by mesityl), 6.28 (3H, s, OMe), 6.51 (2H, d, *J* 2 Hz, CH₂), 7.69 (3H, s, *p*-Me), and 8.05 (6H, s, *o*-Me) [olefinic to methylene absorptions in the ratio 1 : 4, indicating a 40% migration of deuterium]. Unchanged ketone (4e) (0.17 g) was recovered.

The benzofulvenes (4) and (5) were identified by their characteristic n.m.r. absorptions and the composition of mixtures was determined from the intensity of the sharp methoxy-absorptions at τ 6.23 and 6.28.

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* We thank Dr. K. Salisbury for checking this experiment.

¹² P. Pfeiffer and E. Milz, *Ber.*, 1938, **71**, 272.