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APPROACHES TO PSEUDOINDENE

PRODUCTS DERIVED FROM THE CARBENES BENZOCYCLOBUTEN-1-YLCARBENE, 2-METHYLBENZOCYCLOBUTENYLIDENE AND *o*-STYRYLCARBENE

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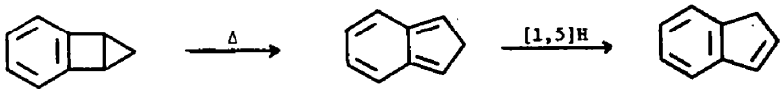
Abstract—The title carbenes, which in principle can all serve as precursors to the reactive hydrocarbon pseudoindene, have been generated by the photolysis of the sodium salts of the tosylhydrazones of (a) benzocyclobutene-1-carboxaldehyde, (b) 2-methylbenzocyclobutenone and (c) *o*-formylstyrene. Indene was formed in reactions (a) and (c): in the former case deuterium labelling experiments suggest a ring expansion mechanism rather than a pseudoindene intermediate. In the latter case deuterium labelling and trapping experiments implicate a symmetrical isoindene intermediate, which can arise either via pseudoindene, or via direct electrocyclic ring closure of *o*-styrylcarbene.

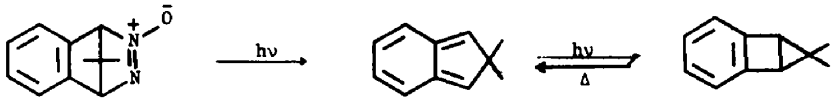
The hydrocarbon pseudoindene (2,3-benzobicyclo-[2.1.0]pent-2-ene) **1** and derivatives of **1** have been postulated as intermediates in a number of chemical transformations.[1-4] It has been inferred that **1** and its derivatives rearrange to the indene **3** ring system, via isoindene **2** intermediates under very mild conditions. This idea has recently been confirmed with the characterisation of the dimethyl substituted pseudoindene **6**, which was generated by irradiation of 2,2-dimethylisoindene **5** (Scheme 2).[5] Thermal rearrangement of **6** → **5** occurred readily at temperatures as low as 0°. Further thermal rearrangement of **5** to give dimethyl substituted indenes was not observed at these low temperatures, due to the relatively poor migratory aptitude of Me vs H in the requisite [1,5]-sigmatropic shift.

The parent pseudoindene molecule **1** has to date not been characterized. The facility with which isoindene **2** rearranged to indene **3** by means of a [1,5] H shift,[6,7] suggests that a synthesis of **1** via **2** would not be feasible. Accordingly, a strategy different to that shown in Scheme 2 is required for any projected synthesis of **1**. It is possible to envisage a number of carbenes which could in principle serve as precursors to **1** (Scheme 3). Thus in the carbenes **7**, **8**, **10** and **11**, insertion of the carbenic centre into one of the indicated C–H bonds would form **1**, as would intramolecular addition to the alkene Π-bond in the unsaturated carbene **9**. We have investigated some of these possibilities and in this paper we describe products formed from benzocyclobuten-1-ylcarbene **7**, 2-methylbenzocyclobutenylidene **8**, and *o*-styrylcarbene **9**. The generation



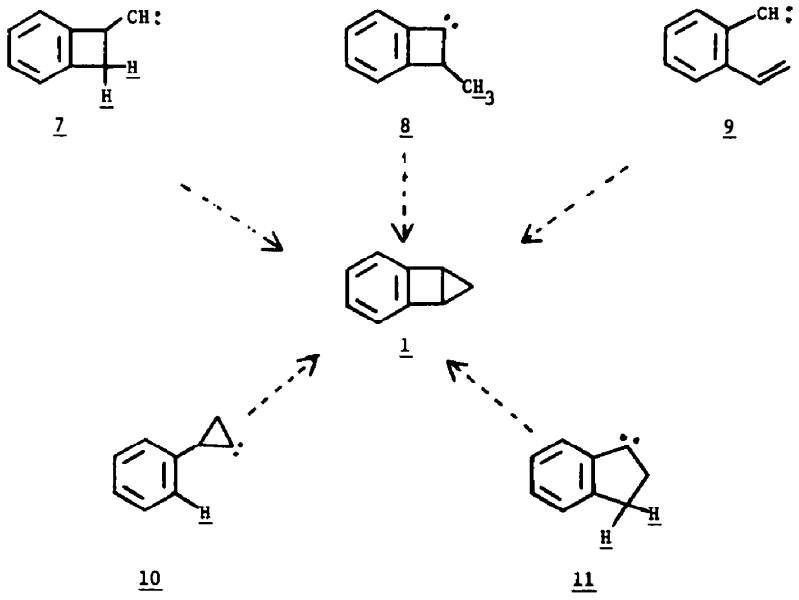
1 2 3

Scheme 1



4 5 6

Scheme 2



Scheme 3

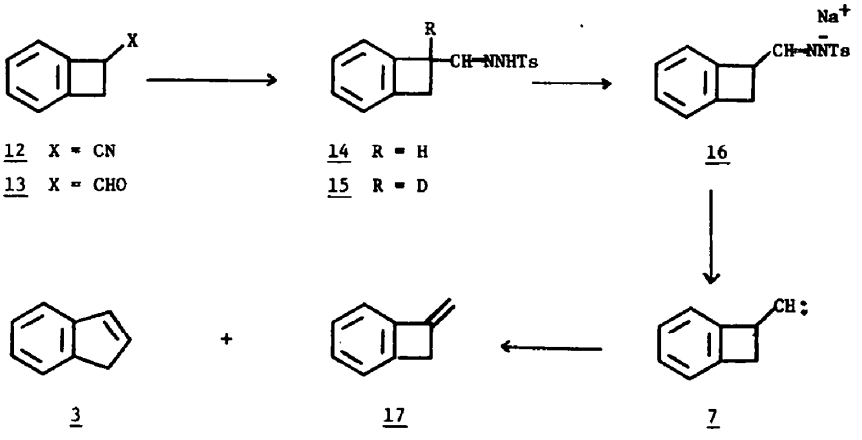
of carbenes **10** and **11** was not investigated, since in each system insertion into an α C–H bond is expected to be the predominant reaction pathway.

RESULTS AND DISCUSSION

Benzocyclobuten-1-ylcarbene 7

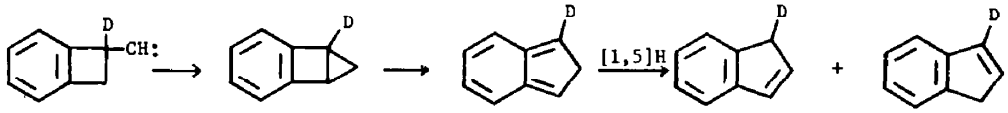
Benzocyclobutene-1-carbonitrile **12** was reduced with diisobutylaluminium hydride in benzene to give benzocyclobutene-1-carboxaldehyde **13**, which was converted into the *p*-toluenesulphonylhydrazone (tosylhydrazone) **14** (Scheme 4). Irradiation of a suspension of the derived sodium salt **16** through Pyrex in THF gave in 88% yield methylenebenzocyclobutene **17** and indene **3** in a ratio of 18:82. The formation of **17** occurs simply by insertion into the α C–H bond in carbene **7**, a common reaction of alkylcarbenes.[8] However, the formation of indene can occur by a number of pathways, and an attempt was made to delineate the mechanism by means of deuterium labelling (Scheme 5). It can be seen that formation of indene from **18** via a pseudoindene intermediate should give a 1:1 mixture of indene-1-D **21** and indene-3-D_1 **22** while simple ring expansion by CH_2 migration should give exclusively **22**, and ring expansion through aryl migration would afford indene-2-D_1 **23**.

The deuterated carbene **18** was generated in a manner analogous to that shown in Scheme 4, except that the nitrile **12** was first deuterated in the α position by treatment with NaOD–D_2O. From NMR and MS evidence, the deuterium content of the precursors through to the tosylhydrazone **15** was >95% D_1. The methylenebenzocyclobutene formed was a mixture of the two isomers **24a** and **24b** as both vinylic proton signals were diminished, that at δ 5.26 representing 0.5 protons, and that δ 4.86 integrating for 0.6 protons. The indene formed was found to contain deuterium in position 2, i.e. consisted mainly of isomer **23** as only the



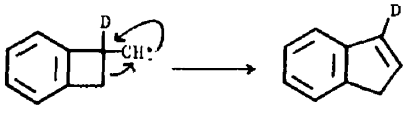
Scheme 4

(a) Pseudoindene intermediate:



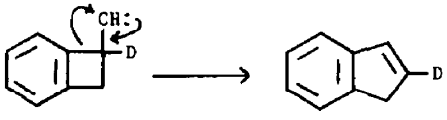
18 19 20 21 22

(b) CH_2 migration:



18 22

(c) Aryl migration:



18 23

Scheme 5

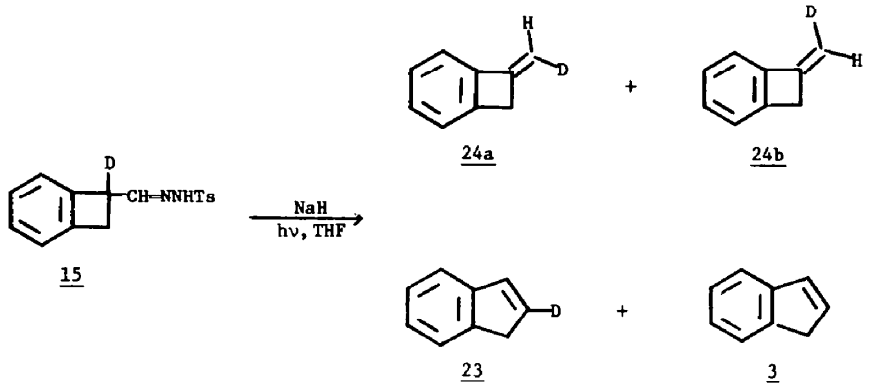
vinyl proton resonance for H2 showed a decrease in intensity. This implicates pathway (c) involving aryl migration as the major rearrangement mechanism. However, careful integration showed that this signal in fact represented 0.42 protons per molecule, or only 0.58 deuterons. As the H1, H3 and aryl signals integrated correctly for two, one and four protons respectively, it must be concluded that the indene is a mixture of undeuterated indene **3** and indene-2-D_1 **23** in a ratio of 42:58, i.e. 42% of the indene molecules have suffered loss of deuterium.

The mass spectrum of unlabelled indene **3** shows peaks at *m/e* 116 (M^+), 115 and 114 in the ratio of 100:88 < 5. Under the same conditions, the deuterated indene produced in the reaction shows peaks at *m/e* 117 (M^+), 116 and 115 in the ratio 91:100:40. If it is assumed that the peak of intensity 40 at *m/e* 115 arises solely from undeuterated indene and not from M^+–D, then the amount of indene-2-D_1 **23** in the product can be calculated to be 56%, similar to the value obtained from integration of the NMR spectrum.

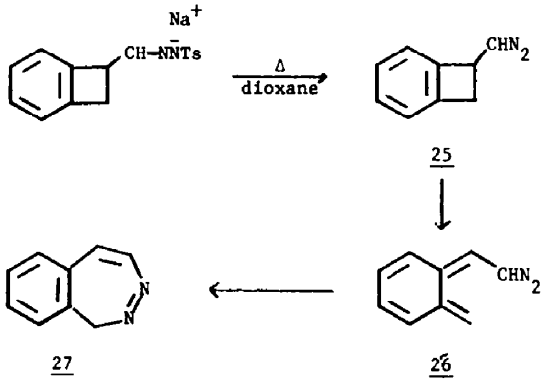
As the methylenebenzocyclobutene **24** appears to be >90% monodeuterated, loss of D from the indene cannot be ascribed to exchange occurring in the tosylhydrazone **15** or its sodium salt in the basic photolysis medium. This presumes of course that both the methylenebenzocyclobutene and indene arise from a common intermediate. Nor does the D loss occur during preparative glc, as the crude mixture also showed the H2 signal in its NMR spectrum. The possibility of the D undergoing scrambling during photolysis as do alkyl[9] and aryl[10,11] group can also be rejected as McCullough[11] has shown that indene 1,1,3-D_3 when irradiated to up to 80% polymerisation still showed no such scrambling.

Another possibility is that one or both of the two other pathways (a) and (b) in Scheme 5 are also operating, giving indene isomers with D in positions 1 and 3, which are known to be susceptible to base-catalysed exchange.[12–14] In a control experiment, a sample of indene-1-D_1 **21** was irradiated in THF in the presence of NaH in an attempt to simulate the reaction conditions to which product labelled in position 1 would be subjected. The reaction mixture was divided and a portion subjected to an aqueous work-up, as used after the tosylhydrazone photolysis, and the remainder was worked up without the addition of water. The indene recovered from both procedures had a benzylic methylene signal in the NMR spectrum integrating for 1.4 protons, indicating that 40% of the D had been lost from the 1 position. No significant amount of deuterium scrambling to the vinylic positions could be detected. Thus the reason for the D loss in the photolysis of tosylhydrazone could be due to the formation of some indene-D_1 but the finding that indene-2-D_1 is the predominant product indicates that its formation proceeds mainly through aryl migration (path (c), Scheme 5).

Thermolysis of the sodium salt of tosylhydrazone **14** in refluxing dioxane was also carried out (Scheme 7). This gave a single product identified as 1H-2,3-benzodiazepine **27** by comparison with an authentic sample.[15] This material presumably arises via electrocyclic ring opening of the diazo compound **25**, the expected initial decomposition product of the tosylhydrazone. The resulting diazo substituted *o*-xylylene **26** can then undergo electrolcyclic ring closure to give the observed product **27**. Sharp *et al.* previously obtained the benzodiazepine **27** by a novel electrocyclic ring closure of *o*-diazoformylstyrene **29**, generated from the salt of the tosylhydrazone **28**.[15]



Scheme 6



Scheme 7

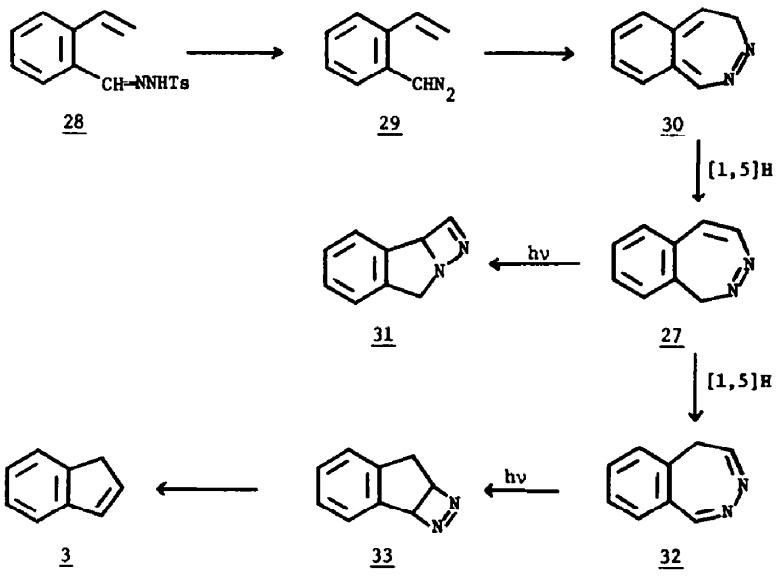
Irradiation of **27** was found to give cleanly the tricyclic isomer **31**.[15] However, **27** is readily isomerised by base into the 5H isomer **32**,[15,17] a compound which can extrude nitrogen on photolysis to give indene, presumably via intermediate **33**.[17] In view of this, the possibility of 1H-2,3-benzodiazepine **27** being an intermediate in the photochemical formation of indene from the salt of tosylhydrazone **14** must be considered. If **27** were to isomerise under the basic photolysis conditions to the 5H isomer **32**, this could lead by a non-carbenic route to indene labelled in the 1-position, a position susceptible to base-catalysed H–D exchange. To investigate this possibility, a sample of 1H-2,3-benzodiazepine **27** was subjected to conditions simulating those used for the photolysis of the sodium salt of the tosylhydrazone **14**. The product obtained from this experiment was almost pure 2a,7-dihydro[1,2]diazeto[4,1-*a*]isoindole **31**, and no indene was formed. It thus appears that the indene formed in the photolysis of the salts of tosylhydrazones **14** and **28** (see below) must arise from carbene precursors, rather than benzodiazepines.

o-*Styrylcarbene* **9**

The thermal decomposition of the sodium salt of tosylhydrazone **28** has already been described[15] and benzodiazepine formation was the only reaction observed (Scheme 8). We find, however, that photolysis of the sodium salt of **28** in THF results in products derived from the carbene **9** (Scheme 9). Thus indene **3** and the solvent insertion products **34**, **35** and **36** were formed. The ratio of indene:**36**:**34** and **35** was 30:1:10 as estimated by glc. The structures of **34** and **35** were evident from spectral data, while the material described as **36** was only obtained in small quantities, and its structure is assumed on the basis that it is isomeric with **34** and **35**. The formation of these solvent-derived products could be suppressed by addition of cuprous chloride to the photolysis mixture; under these conditions up to 73% of the theoretical amount of indene was formed, and the ratio of indene: solvent insertion product rose to 9:1.

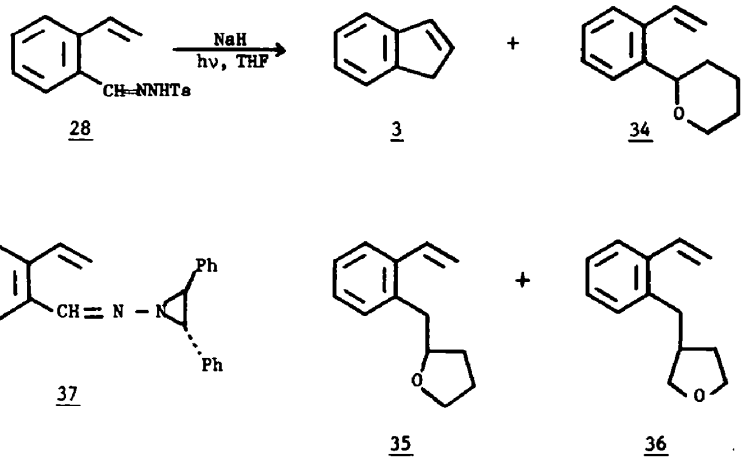
Carbenes have also been generated by the thermolysis of aziridinylimine derivatives of aldehydes.[18,19] Accordingly, **37** was prepared, and its thermolysis was found to also yield indene in 52% yield.

The formation of indene from *o*-styrylcarbene can be explained in terms of a number of mechanisms which are illustrated for the deuterated carbene **38** in Scheme 10. Photolysis of the sodium salt of the deuterated analogue of tosylhydrazone **28** in the presence of cuprous chloride was therefore carried out; this gave indene in 40% yield. The NMR spectrum of



28 29 30 31 27 32 33 3

Scheme 8



28 3 34 37 35 36

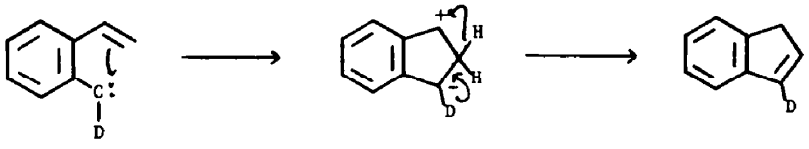
Scheme 9

this product showed the signals for H1 and H3 to be diminished, integrating for 1.45 and 0.64 protons, i.e. 0.55 and 0.36 deuterons. This suggests that the product is a mixture of indene-1-D_1 **21**, indene-3-D_1 **22** and undeuterated indene in the ratio of 55:36:9. Assuming that base-catalysed equilibration of indene under the reaction conditions does not occur to a significant extent,† this label distribution is consistent with a mechanism proceeding predominantly through a symmetrical intermediate, i.e. either pathway (b) involving pseudoindene or pathway (c) leading directly to isoindene. A number of possible combination of pathways (a)–(d) can be envisaged to give the observed label distribution. However, photochemical generation of carbene **9** in the presence of a 1.5 fold excess of dimethyl fumarate gave the adduct **39** in 20% yield. This demands the intermediacy of an isoindene intermediate, and provides compelling evidence for pathways (b) and/or (c). As indene was also isolated from this reaction in 25% yield, mechanisms (a) and (d) are not precluded as competing pathways. However, it is also possible that this indene arises because the dimethyl fumarate does not intercept all of the isoindene intermediate at the relatively low (10^{-2} M) concentration of reactants used. Adduct **39** could also be isolated in 9% yield when the aziridinylimine **37** was decomposed thermally in the presence of dimethyl fumarate.

We conclude that we have demonstrated the existence of a symmetrical isoindene intermediate in the formation of indene from *o*-styrylcarbene. This

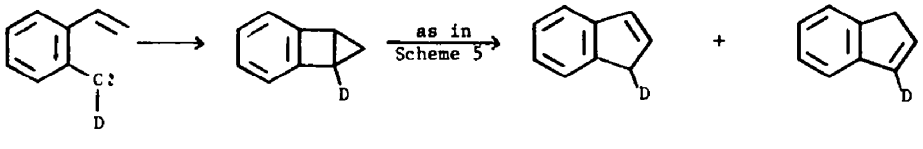
†This assumption is reasonable since the photochemical decomposition of the salt of **28** was quite rapid (0.25 hr) while in the previous control experiment, indene-1-D, underwent D loss to the extent of *ca* 40% when subjected to similar conditions for a longer reaction time (1.75 hr).

(a) Zwitterion formation followed by hydride migration:



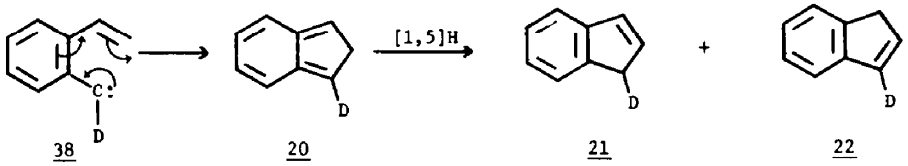
38 39 22

(b) Addition to double bond - pseudoindene intermediate:



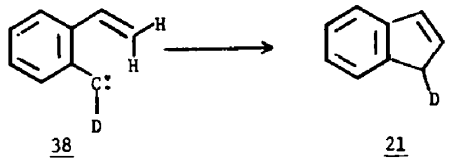
38 39 21 22

(c) Electrocyclic ring closure:



38 20 21 22

(d) Insertion into the vinylic C–H bond:



38 21

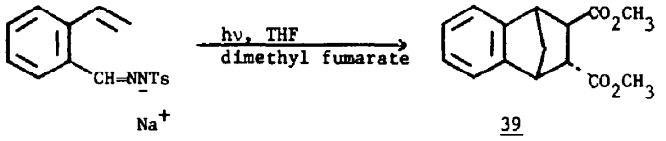
Scheme 10

intermediate can arise through pathways (b) and/or (c) (Scheme 10). An exact analysis of total reaction scheme is rather difficult, due to the problem of carrying out unambiguous control experiments to check the scrambling or loss of D label in the indene produced.

2-Methylbenzocyclobutenylidene **8**

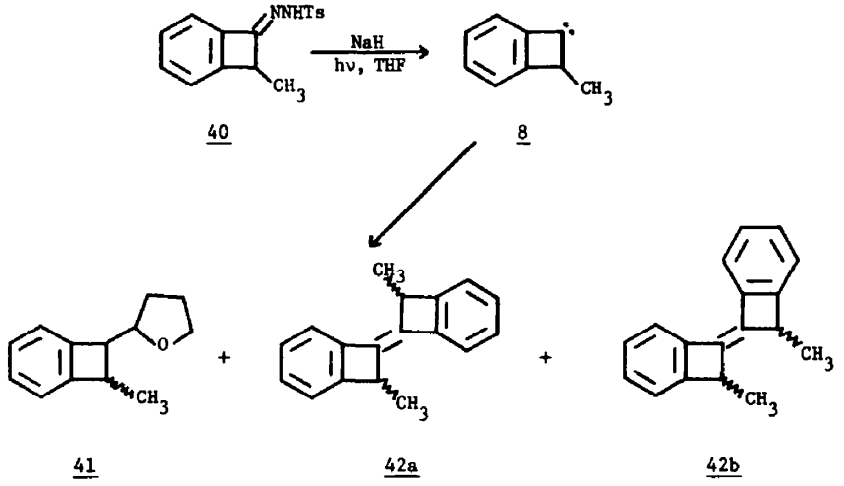
Photolysis of the sodium salt of 2-methylbenzocyclobutenone tosylhydrazone **40** in THF failed to produce any indene. Instead the solvent insertion product **41** and the dimer mixture **42** were isolated in yields of 14% and 32% respectively. Compound **41** was readily recognised by a base peak at *m/e* 71 in the mass spectrum, corresponding to the tetrahydrofuranyl moiety. Its NMR spectrum showed two Me doublets of equal size, indicating that the product was an equal part mixture of *cis* and *trans* isomers. The NMR spectrum of the dimer mixture showed four Me doublets, suggesting the presence of the four possible diastereomers. Analogous dimer formation has previously been observed in the photolysis of the sodium salt of 4,6-dimethylbenzocyclobutenone tosylhydrazone.[20]

The formation of the products **41** and **42** clearly implicates the intermediacy of 2-methylbenzocyclobutenylidene **8**. However, intermolecular reactions of **8** appear to be favoured over intramolecular rearrangements, and in particular over insertion into the Me C–H bonds. As a model reaction we investigated the decomposition of the sodium salt of 2,2-dimethylindan-1-one tosylhydrazone **43**. This afforded **45** as the only hydrocarbon product under both thermolysis and photolysis conditions, indicating that in 2,2-dimethylindan-1-ylidene **44** insertion into one of the adjacent Me groups occurs readily. The failure of 2-methylbenzocyclobutenylidene **8** to yield pseudoindene in an analogous reaction may be a consequence of ring strain effects. In the more strained 4-membered ring of **8**, the Me group is bent away from the adjacent carbene centre compared to **44**. Insertion into the Me C–H bond is therefore not competitive with



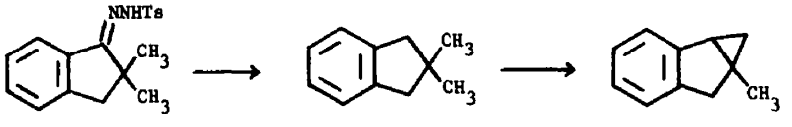
39

Scheme 11



40 8 41 42a 42b

Scheme 12



43 44 45

Scheme 13

intermolecular reactions of the carbene **8**. Intramolecular Me insertion is also favoured statistically in the model system **44** by the presence of two proximate Me groups.

The thermal decomposition of the sodium salt of 2-methylbenzocyclobutenone tosylhydrazone **40** in refluxing THF proceeded very sluggishly, and only the C–H insertion product **41** was observed to form. Change of the solvent to benzene, which is less prone to C–H insertion, resulted in addition of the carbene to the aromatic Π-system to give a novel rearranged product which is discussed in the accompanying paper.[21] Thus intramolecular insertion to give pseudoindene is clearly not a favoured reaction pathway of 2-methylbenzocyclobutenylidene.

EXPERIMENTAL

M.ps and b.ps are uncorrected, and b.ps of small quantities of liquids refer to bath or heating block temps. Microanalyses are by the Australian Microanalytical Service, Melbourne. NMR spectra were recorded with Hitachi Perkin–Elmer R24B (60 Mz) or Bruker HX90 (90 Mz) instruments. Mass spectra were measured using a Varian MAT CH7 instrument, with an inlet temp of 25° and an ionisation energy of 70 eV unless otherwise stated. IR spectra were recorded with a Perkin–Elmer 283 spectrophotometer, and electronic spectra

with a Beckman Acta MIV instrument. Analytical glc was performed using a Perkin–Elmer 880 or Varian 1800 gas chromatograph using N_2 as carrier gas, while preparative glc was carried out with a Wilkins Aerograph 700 Autoprep, using He as carrier gas. The following columns were used: A 10′ × 1/8″ stainless steel column packed with 3% SE30 on 80–100 mesh Chromosorb W; B 10′ × 1/8″ copper column packed with 5% Carbowax 20M on 80–100 mesh Chromosorb W; C 10′ × 3/8″ aluminium column packed with 10% Carbowax 20M on 60 80 mesh Chromosorb W; D 9′ × 3/8″ aluminium column packed with 10% SE30 on 60–100 mesh Chromosorb W.

Irradiations were carried out through a water-cooled Pyrex immersion well using a Philips HPK 125 high pressure mercury lamp. Gas evolution was followed by passing the exit gases from the static irradiation vessel through a $CaCl_2$ tube into an inverted burette filled with water. Solvents for photolyses and thermolyses were redistilled from LAH under dry, O_2-free N_2 before use. Organic extracts were dried over anhyd $MgSO_4$.

Benzocyclobutene-1-carboxaldehyde p-*toluenesulphonylhydrazone* **14**

A soln of diisobutylaluminium hydride (5.5 g, 39 mmol) in benzene (50 ml) was added dropwise under N_2 to a stirred soln of **12** (3.4 g, 26 mmol) in benzene (10 ml). The mixture was stirred for 1.5 hr and the excess of reducing agent was destroyed by the addition of MeOH, followed by H_2O. The mixture was worked up by ether extraction, and the extract was washed thrice with 3% HCl, water and was dried and evaporated to give the *aldehyde* **13** as an unstable oil (1.2 g, 34%). A small amount was distilled at 47°/0.03 mm. NMR (CCl_4) δ: 9.7 (d, J 3.5 Hz, 1 H, CHO), 7.5–6.8 (m, 4 H, ArH), 4.13 (q, 1 H, methine), 3.37 (d, 2 H, methylene). MS (50°): 132 (M^+, 80%), 131 (28), 104 (20), 103 (100), 102 (14), 77 (70). A soln of the above aldehyde (950 mg, 7.2 mmol) and tosylhydrazine (1.34 g, 7.2 mmol) in the minimum volume of MeOH was kept at 0° for 12 hr. The precipitate (1.84 g) was recrystallised from aqueous MeOH to give the *tosylhydrazone* **14** as colourless crystals (1.6 g, 74%), m.p. 115° (dec). (Found: C, 64.0; H, 5.4. $C_{16}H_{16}N_2O_2S$ requires: C, 64.0; H, 5.4%). NMR ($CDCl_3$) δ: 8.05–7.56 (m, 3 H, 2 × ArH and NH), 7.36–6.8 (m, 7 H, 6 × ArH and CH=N), 4.5–4.0 (m, 1 H, methine), 3.84–2.84 (m, 2 H, methylene). MS (80°, 45 eV): 157 (5%), 156 (9), 145 (100), 144 (4), 128 (27), 118 (9), 117 (15), 116 (45), 115 (55), 92 (27), 91 (45).

Photolysis of the sodium salt of benzocyclobutene-1-carboxaldehyde p-*toluenesulohonylhydrazone* **14**

NaH (65 mg of 80%, 2.1 mmol) was added to a soln of **14** (500 mg, 1.66 mmol) in THF (50 ml) and the resulting suspension stirred for 15 min under N_2. More THF (200 ml) was added and the mixture cooled in ice and irradiated until gas evolution ceased (25 ml after 3 hr). The THF was evaporated under reduced pressure and the residue taken up in ether and washed with H_2O. Evaporation of the dried extract gave an oil (170 mg, 88%), which by NMR and glc (column A, 120°, column B, 120°) showed the presence of two components in the ratio of 18:82. Preparative glc (column C, 140°) gave *methylenebenzocyclobutene* **17**.[23] NMR (CCl_4) δ: 7.15 (s, 4 H, ArH), 5.25 (brs, 1 H, vinyl), 4.88 (brs, 1 H, vinyl), 3.60 (brs, 2 H, methylene) similar to that reported.[24] UV (EtOH) λ_{max} 219 (log ε 4.31), 244 (4.78), 252 (4.72), 280 (4.0), 287 (4.1), 296 (4.3); followed by *indene* **3**, NMR (CCl_4) δ: 7.03–7.55 (m, 4 H, ArH), 6.95–6.76 (m, 1 H, H3), 6.60–6.38 (m, 1 H, H2), 3.33 (narrow m, 2 H, methylene). MS: 116 (M^+, 100), 115 (88), 89 (16).

Benzocyclobutene-1-carboxaldehyde-1-D$_1$ p-*toluenesulphonylhydrazone* **15**

The nitrile **12** was added to a soln of NaOD prepared from Na (40 mg) and D_2O (5 ml) in THF (40 ml). The mixture was refluxed for 1.5 hr, poured into water and worked up by ether extraction. Distillation gave *benzocyclobutene-1-carbonitrile-1-D*$_1$ as a clear oil (1.66 g, 82%), b.p. 64–8°/0.3 mm. NMR δ: 6.85–7.40 (m, 4 H, ArH), 3.55 (d, 2 H, methylene). The methine signal intensity was too low to be accurately integrated. The above nitrile (1.5 g, 11.5 mmol) was reduced using diisobutylaluminium hydride (3 g, 21.1 mmol) in benzene as before to give *benzocyclobutene-1-carboxaldehyde-1-D*$_1$ (1.5 g, 98%). NMR (CCl_4) δ: 9.70 (s, 1 H, CHO), 7.40–6.90 (m, 4 H, ArH), 3.4 (s, 2 H, methylene). MS (50°): 133 (M^+, 86%), 132 (43), 131 (8), 105 (24), 104 (100), 103 (29), 102 (5), 78 (40). The above aldehyde (1.2 g, 9 mmol) was treated with tosylhydrazine (1.6 g, 8.6 mmol) in MeOH as before to give the *deuterated tosylhydrazone* **14** as colourless crystals (1.3 g, 48%). NMR ($CDCl_3$) δ: 8.0–8.5 (br m, 1 H, NH, exchangeable), 7.85–7.55 (d, 2 H, ArH), 7.38–6.75 (m, 7 H, 6 × ArH and CH=N), 3.4 and 3.0 (ABq, J 14 Hz, 2 H, methylene), 2.38 (s, 3 H, $ArCH_3$). MS (80°, 45 eV): 147 (9%), 146 (100), 145 (18), 119 (15), 118 (14), 117 (24), 116 (33), 115 (11), 91 (18).

Photolysis of the sodium salt of benzocyclobutene-1-carboxaldehyde-1-D$_1$ p-*toluenesulphonylhydrazone* **15**

This was carried out in the same manner as for **14** using deuterated **15** (340 mg, 1.13 mmol), NaH (60 mg, 2 mmol) in THF (150 ml). Irradiation was stopped when gas evolution had ceased (34 ml after 1.5 hr). Work-up as before gave an oil (140 mg) shown by glc (column A, 120°) to contain methylenebenzocyclobutene and indene in a ratio of 19:81. Preparative glc (column C, 140°) gave *methylenebenzocyclobutene-β-D*$_1$ (24). NMR (CCl_4) δ: 7.18 (s, 4 H, ArH), 5.26 (m, 0.5 H, vinyl), 4.86 (m, 0.6 H, vinyl), 3.63 (narrow m, 2 H, methylene). Signal areas were the average of five integrals. The second component eluted was *indene-2-D*$_1$ **23**, NMR (CCl_4) δ: 7.5–7.05 (m, 4 H, ArH), 6.82 (m, 0.97 H, H3), 6.50 (m, 0.42 H, H2), 3.33 (narrow m, 1.98 H, H1). Signal areas were the average of nine integrals. MS: 117 (12%), 116 (100), 115 (88), 89 (22).

Preparation of indene-1-D$_1$[7] **21**

A soln of indene (1.2 g, 10.4 mmol) in benzene (15 ml) was added dropwise under N_2 to a stirred pentane soln of n-BuLi (10.6 mmol). A thick white ppt formed and the mixture was heated at 60° for 5.5 hr. D_2O (8 ml) was added, followed by anhyd ether (10 ml). The layers were separated, and the aqueous layer was re-extracted with ether. The combined organic extracts were washed with H_2O, NaCl aq dried and evaporated. Distillation under reduced pressure gave *indene-1-D*$_1$ as an oil (537 mg, 44%). NMR (CCl_4) δ: 7.4–6.95 (m, 4 H, ArH), 6.57 (d, 1 H, H3), 6.27 (d, 1 H, H2), 3.18 (brs, 1 H, H1). MS: 118 (12%), 117 (M^+, 100), 116 (78), 115 (19), 90 (10), 89 (10).

Control experiment

Irradiation of indene-1-D$_1$. NaH (24 mg, 0.67 mmol) was added to a soln of indene-1-D$_1$ (170 mg, 1.45 mmol) in THF under N_2. The mixture was stirred for 5 min, and then cooled in an ice-water bath and irradiated for 1.75 hr. The THF was evaporated under reduced pressure and the residue treated with light petroleum (10 ml). To 5 ml of this soln was added ether and water, and extraction in the usual way gave the labelled indene as a pale yellow oil (83 mg). NMR (CCl_4) δ: 7.55–7.0 (m, 4 H, ArH), 6.95–6.76 (m, 1 H, H3), 6.60–6.38 (m, 1 H, H2), 3.25 (brs, 1.40 H, H1). The other 5 ml of the solution was filtered through a small column of activity II Al_2O_3 in light petroleum to give indene as a colourless oil (84 mg). The NMR spectrum also showed the H1 benzylic signal to represent 1.4 protons.

Thermolysis of the sodium salt of benzocyclobutene-1-carboxaldehyde p-*toluenesulphonylhydrazone* **14**

NaH (35 mg, 1.17 mmol) was added to a soln of (294 mg, 1.0 mmol) in dioxane (40 ml) under N_2. The mixture was stirred at room temp for 20 min and then refluxed for 30 min. The mixture was poured into water and worked up by ether extraction to give a yellow oil (100 mg), shown by NMR of the

essentially pure 1 H-2,3-*benzodiazepine* **27**.[15] Sublimation at 45°/0.03 mm gave yellow crystals, m.p. 49° (lit.[15] 49–50°).

Preparation of authentic 1 H-2,3-*benzodiazepine* **27**

This method was based on that used by Sharp *et al.*[15] NaH (85 mg, 2.93 mmol) was added to a soln of 2-formylstyrene tosylhydrazone (729 mg, 2.43 mmol) in THF (15 ml) under N_2. The resulting clear yellow soln was stirred at room temp for 16 min, and then more THF (50 ml) was added, and the flask immersed in an oil bath at 100°. After 25 min the mixture, which was bright yellow and contained a thick white ppt, was filtered. Evaporation of the filtrate gave **27** as a yellow-orange solid (360 mg), whose NMR spectrum was identical with that reported.[15] As previous attempts to sublime this material had produced only a small quantity of crystals, m.p. 49°, with the formation of a dark viscous residue, the crude product was used for the irradiation experiment below.

Control experiment

Irradiation of 1 H-2,3-*benzodiazepine* **27**. A mixture of NaH (45 mg, 1.5 mmol), sodium *p*-toluenesulphinate (225 mg, 1.2 mmol) and the diazepine **27** (180 mg, 1.25 mmol) in THF (75 ml) was stirred under N_2 for 10 min at room temp and then cooled in ice and irradiated for 1.5 hr. No gas was evolved. The mixture was concentrated, diluted with water and worked up by ether extraction to give an orange oil (118 mg). The spectral data (NMR and MS) were in accord with those published[16] for 2a,7-dihydro[1,2]diazeto[4,1-a]isoindole **31**.

2-*Formylstyrene* p-*toluenesulphonylhydrazone* **28**

A soln of 2-formylstyrene[25] (2.86 g, 21.6 mmol) and tosylhydrazine (4 g, 21.6 mmol) in MeOH containing a few drops of 3% HCl was kept at room temp. overnight. The ppt was filtered and recrystallised from MeOH to give **28** as colourless crystals (4.6 g, 71%), m.p. 115° (lit.[15] 115–16°). NMR ($CDCl_3$) δ: 8.38 (brs, 1 H, NH), 8.1–7.5 (m, 3 H, 2 × ArH and CH=N), 7.45–7.05 (m, 6 H, ArH), 7.1–6.7 (X part of ABX, 1 H, vinyl), 5.6–5.2 (AB part of ABX, 2 H, vinyl), 2.37 (s, 3 H, $ArCH_3$). MS (80°): 300 (M^+, 17%), 299 (8), 156 (12), 146 (10), 145 (69), 144 (17), 118 (12), 117 (19), 116 (57), 115 (100), 92 (26), 91 (54).

Photolysis of the sodium salt of 2-formylstyrene p-*toluenesulphonylhydrazone*

NaH (60 mg, 2 mmol) was added to a soln of **28** (500 mg, 1.67 mmol) in THF (20 ml) under N_2. The mixture was stirred for 15 min, after which more THF (100 ml) was added and the mixture cooled in ice and irradiated until gas evolution ceased (1 hr). The THF was removed under vacuum and the residue treated with H_2O and worked up by ether extraction to give an oil (190 mg). Glc (column A, 90° → 140° at 10° min^{-1}) showed three peaks in the ratio 30:1:10. These were separated by preparative glc (column D, 160°) to give (i) indene (40 mg, 21%); (ii) a trace of colourless oil, tentatively identified as **36**: MS (80°): 188 (M^+, 50%), 159 (40), 132 (56), 117 (40), 115 (35), 104 (30), 91 (50), 71 (100); (iii) a mixture of two components which were separated by preparative tlc to give 2-(2′-*styryl*)*tetrahydropyran* **34** (25 mg, 8%). (Found: C, 83.2; H, 8.5. $C_{13}H_{16}O$ requires: C, 82.9; H, 8.6%). NMR (CCl_4) δ: 7.9–7.0 (m, 4 H, ArH), 6.98 (X part of ABX partly obscured by ArH, 1 H, vinyl), 5.52 (B part of ABX, J_{trans} 17.5 Hz, 1 H, vinyl), 5.22 (A part of ABX, J_{cis} 11 Hz, J_{gem} 1.5 Hz, 1 H, vinyl), 4.6–3.85 and 3.7–3.2 (m, 3 H, CH_2O and methine), 2.1–1.1 (brm, 6 H, methylene). MS: 188 (M^+, 50%), 159 (60), 145 (30), 133 (45), 132 (100), 131 (40), 129 (30), 117 (25), 115 (45), 104 (90), 103 (45), 91 (14), 77 (50). The second component was 2-(2′-*vinylbenzyl*)-*tetrahydrofuran* **35** (14 mg, 5%). (Found: M, 188.1220. $C_{13}H_{16}O$ requires: 188.1202). NMR: 7.5–6.9 (m, 4 H, ArH), 7.02 (X part of ABX, partly obscured, 1 H, vinyl), 5.54 (B part of ABX, J_{trans} 17.5 Hz, 1 H, vinyl), 5.22 (A part of ABX, J_{cis} 11 Hz, J_{gem} 2 Hz, 1 H, vinyl), 4.1–3.4 (m, 3 H, $CHOCH_2$), 2.88 and 2.79 (d of ABq, J_{AB} 14 Hz, J_{cic} 6 Hz, 2 H, benzylic methylene), 2.0–1.3 (brm, 4 H, ring methylene). MS: 188 (M^+, 22%), 117 (10), 115 (15), 91 (10), 71 (100), 43 (65).

Photolysis of the sodium salt of 2-formylstyrene p-*toluenesulphonylhydrazone* **28** *in the presence of* Cu_2Cl_2

NaH (60 mg, 2 mmol) was added to a stirred soln of **28** (520 mg, 1.73 mmol) in THF (20 ml) under N_2. After 15 min, Cu_2Cl_2 (50 mg, 0.5 mmol) and more THF (150 ml) were added and the mixture was cooled in ice and irradiated until gas evolution ceased (40 min). Work-up in the usual manner gave an oil (170 mg), shown by NMR and glc to consist almost entirely of indene together with minor amounts of **34** and **35**. Glc analysis of an aliquot of the crude reaction product using tetralin as internal standard, showed the yield of indene to be 73%.

Preparation of o-(trans-2,3-*diphenylaziridin*-1-*yliminomethyl*-)*styrene* **37**

A soln of 1-amino-2,3-diphenylaziridine[18,26] (500 mg, 2.3 mmol) and *o*-formylstyrene (300 mg, 2.3 mmol) in ether (10 ml) was kept at 0° overnight. The mixture was diluted with light petroleum, and the resulting ppt filtered and recrystallised (ether–light petroleum) to give the *aziridine* **37** (560 mg, 76%) as colourless needles, m.p. 83–4° (dec.). (Found: C, 85.4; H, 6.2. $C_{23}H_{20}N_2$ requires: C, 85.2; H, 6.2%). NMR ($CDCl_3$) δ: 8.3 (s, 1 H, CH=N), 7.44–6.93 (m, 14 H, ArH), 6.64 (X part of ABX, 1 H, vinyl), 5.32 (B part, J_{trans} 17 Hz, 1 H, vinyl), 5.10 (A part, J_{cis} 11 Hz, J_{gem} 2 Hz, 1 H, vinyl), 3.59 (brs, 2 H, aziridine). MS (30°): 194 (36%), 180 (96), 179 (68), 178 (40), 165 (32), 144 (20), 116 (42), 116 (42), 116 (42), 115 (100).

Decomposition of the azirinylimine **37**

(a) A stirred mixture of the imine **37** (410 mg) and Cu_2Cl_2 (50 mg) in ether (180 ml) was cooled in an icebath and irradiated under N_2 for 1 hr. The mixture was concentrated, diluted with pentane, filtered, and the filtrate evaporated to give a solid residue. The NMR spectrum of this crude material showed the presence of indene, *cis* and *trans*-stilbene and some starting material. Glc analysis of an aliquot of a solution of the product using phenanthrene as internal standard showed the yield of indene to be 38%. The indene was separated by preparative tlc and identified by its NMR spectrum.

(b) A mixture of the imine **37** (310 mg) and Cu_2Cl_2 (50 mg) in cyclohexane (50 ml) was refluxed under N_2 for 18 hr. The mixture was filtered and evaporated to give a residue (200 mg) containing by NMR analysis only indene and *trans*-stilbene. Quantitative glc analysis showed the yield of indene to be 52%.

(c) A soln of the imine **37** (100 mg, 0.31 mmol) and dimethyl fumarate (133 mg, 0.95 mmol) in cyclohexane (25 ml) containing Cu_2Cl_2 (20 mg) was refluxed under N_2 for 12 hr. The soln was filtered and evaporated to give a yellow residue (226 mg). Quantitative glc showed the yield of indene to be 26% and that of adduct **39** (see below) to be 9%.

Preparation of o-(*formyl*-D_1)*styrene* p-*toluenesulphonylhydrazone*

To the Grignard reagent prepared from *o*-bromostyrene (1.14 g, 6.25 mmol) and Mg (150 mg, 6.25 mmol) in THF (20 ml) under N_2 was slowly added dimethylformamide-D_7 (500 mg, 6.25 mmol) in THF (5 ml). The mixture was stirred at room temp for 2 hr, and hydrolysed by the addition of H_2O. Work-up by ether extraction gave essentially pure o-(*formyl*-D_1)*styrene* (680 mg, 82%). NMR (CCl_4) δ: 7.9–7.25 (m, 5 H, 4 × ArH and vinyl), 5.64 (B part of ABX, J_{trans} 17 Hz, 1 H, vinyl), 5.46 (A part, J_{cis} 11 Hz, J_{gem} 2 Hz, 1 H, vinyl). MS: 133 (M^+, 100%), 132 (23), 131 (5), 106 (10), 105 (84), 104 (65), 103 (30), 102 (10), 77–79 (45). The above aldehyde (320 mg, on treatment with tosylhydrazine as before gave the *deuterated tosylhydrazone* (440 mg, 61%), m.p. 112°. NMR ($CDCl_3$) δ: 8.6 (brs, 1 H, NH), 7.9–7.0 (m, 5 H, vinyl + ArH), 5.53 (B part

of ABX, J_{trans} 18 Hz, 1 H, vinyl), 5.33 (A part of ABX, J_{cis} 11 Hz, J_{gem} 2 Hz, 1 H, vinyl), 2.37 (s, 3 H, $ArCH_3$). MS (90°): 302 ($M^+ + 1$, 4%), 301 (14), 300 (8), 156 (10), 147 (11), 146 (86), 145 (13), 119 (27), 118 (97), 117 (60), 116 (100), 115 (16), 92 (40), 91 (50).

Photolysis of the sodium salt of 2-(*formyl*-D_1)*styrene* p-*toluenesulphonylhydrazone*

NaH (40 mg, 1.33 mmol) was added to a stirred soln of the labelled tosylhydrazone (385 mg, 1.28 mmol) in THF (15 ml) under N_2. After 15 min, Cu_2Cl_2 (40 mg) and more THF (80 ml) were added, and the mixture cooled in ice and irradiated until gas evolution ceased (20 min). Work-up as usual gave a brown oil (140 mg) which was filtered through a Al_2O_3 in light petroleum to give a mixture of the deuterated indenes (63 mg, 40%). NMR δ: 7.5–6.88 (m, 4 H, ArH), 6.79 (m, 0.64 H, H 3), 6.44 (m, 1 H, H 2), 3.24 (d, 1.45 H, H 1). The peak areas were the average of size integrals. MS: 118 ($M^+ + 1$), 12%), 117 (100), 116 (81), 115 (19), 90 (12), 89 (10).

Photolysis of the sodium salt of **28** *in the presence of* Cu_2Cl_2 *and dimethyl fumarate*

NaH (70 mg, 2.33 mmol) was added to a stirred soln of **28** (580 mg, 1.93 mmol) in THF (10 ml). After 20 min, dimethyl fumarate (580 mg, 1.93 mmol), Cu_2Cl_2 (60 mg) and more THF (140 ml) were added, and the mixture irradiated as previously until gas evolution ceased (30 min). Work-up in the usual way gave a semi-solid (540 mg) glc analysis (column A, 90 → 250° at 10° min^{-1}) showed the presence of indene, dimethyl fumarate and another peak at longer retention time. Chromatography over Al_2O_3 (25 g) gave in order of elution indene (60 mg, 27%), dimethyl fumarate (80 mg) and the *adduct* **39** (100 mg, 20%). Recrystallisation from aqueous MeOH gave *dimethyl* 1,4-*methano*-1,2,3,4-*tetrahydronaphthalene*-trans-2,3-*dicarboxylate* **39** as colourless crystals, m.p. 64–6° (lit.[27] 67°). NMR ($CDCl_3$) δ: 7.35–7.08 (m, 4 H, ArH), 3.85–3.6 (m, 3 H, *exo* H and bridgeheads), 3.77 (s, 3 H, ester), 3.52 (s, 3 H, ester), 2.87 (d of d, 1 H, *endo* H), 1.91 (m, 2 H, methylene).

2-*Methylbenzocyclobutenone* p-*toluenesulphonylhydrazone* **40**

A soln of 2-methylbenzocyclobutenone[28] (1.98 g, 15 mmol) and tosylhydrazine (2.56 g, 13.8 mmol) in MeOH (10 ml) and a few drops of 3% HCl was kept at room temp for 24 hr, cooled and the ppt collected. Recrystallisation from aqueous MeOH gave the *tosylhydrazone* **40** as prisms (2.3 g, 56%), m.p. 125–135°. (Found: C, 64.2; H, 5.5. $C_{16}H_{16}N_2O_2S$ requires: C, 64.0; H, 5.4%). NMR ($CDCl_3$) δ: 8.1–7.6 and 7.5–7.0 (m, total 9 H, ArH and NH), 4.2–3.8 (m, 1 H, methine), 2.38 (s, 3 H, $ArCH_3$), 1.45 and 1.35 (2 × d, J = 6 Hz, total 3 H, methyl). From this spectrum, the product is a mixture of *syn* and *anti* isomers. MS (100°): 300 (M^+, 4%), 299 (3), 284 (14), 155 (12), 145 (11), 130 (100), 116 (25), 115 (37), 103 (20), 91 (40), 77 (20). λ_{max} (EtOH) 206 (log ε 3.61), 264 (3.33), 294 (3.30).

Photolysis of the sodium salt of 2-*methylbenzocyclobutenone* p-*toluenesulphonylhydrazone*

NaH (60 mg, 2 mmol) was added to a stirred soln of **40** (400 mg, 1.33 mmol) in THF (20 ml) under N_2. After 15 min more THF (150 ml) was added and the mixture cooled and irradiated until gas evolution ceased (20 min). Work-up by removal of the THF and ether extraction gave an oil (160 mg). Preparative tlc gave (i) E *and* 2-*bis*(2-*methylbenzocyclobutenylidene*) **42** (50 mg, 32%), which crystallised from EtOH as needles, m.p. 97–147°. (Found: C, 93.4; H, 6.9. $C_{18}H_{16}$ requires: C, 93.1; H, 6.9%). NMR (CCl_4) δ: 7.4–6.9 (m, 8 H, ArH), 4.05 and 4.03 (2 × q, J 7 Hz, total 2 H, methine), 1.60, 1.58, 1.57, 1.54, 1.52, 1.49, 1.47 (lines of 4 × d, total 6 H, methyl). MS: 232 (M^+, 95%), 217 (80), 216 (50), 215 (80), 202 (80), 117 (100). λ_{max} (EtOH) 206 (log ε 4.41), 280 (427), 311 (4.61), 326 (4.75). (ii) 2-(2′-*methylbenzocyclobuten*-1-yl)*tetrahydrofuran* **41** (34 mg, 14%) as a colourless oil, b.p. 70°/0.05 mm (Found: C, 82.6; H, 8.6. $C_{13}H_{16}O$ requires C, 82.9; H, 8.6%). NMR (CCl_4) δ: 7.21–6.82 (m, 4 H, ArH), 4.11–3.5 (m, 3 H, $CHOCH_2$), 3.23 (m, 1 H, H2′), 2.97 (d of d, 1 H, H 1), 2.13–1.5 (m, 4 H, methylene), 1.41 and 1.38 (2 × d, J 7 Hz, total 3 H, methyl). MS: 188 (M^+, 16%), 172 (8), 170 (8), 143 (28), 129 (30), 117 (35), 115 (40), 104 (15), 91 (30), 71 (100), 43 (40). (iii) a mixture of unidentified polar materials (30 mg).

2,2-*Dimethylindan*-1-*one* p-*toluenesulphonylhydrazone* **43**

A soln of 2,2-dimethylindan-1-one[29] (2 g, 12.4 mmol) and tosylhydrazine (2.3 g, 12.4 mmol) in MeOH (20 ml) and several drops of 1% HCl was refluxed for 2 hr and then kept at room temp for 12 hr. Crystallisation was induced by addn of H_2O and cooling. Recrystallisation from aqueous MeOH gave the *tosylhydrazone* **43** (2.5 g, 62%) as prisms, m.p. 141°. (Found: C, 65.7; H, 6.1. $C_{18}H_{20}N_2O_2S$ requires: C, 65.8; H, 6.1%). NMR ($CDCl_3$) δ: 8.1–7.8 and 7.5–7.2 (m, total 8 H, ArH), 2.83 (s, 2 H, methylene), 2.45 (s, 3 H, $ArCH_3$), 1.2 (s, 6 H, methyl). MS (40°): 328 (M^+, 35%), 173 (30), 157 (5), 144 (100), 129 (50), 117 (5), 116 (5), 115 (5), 91 (50).

Decomposition of the sodium salt of 2,2-*dimethylindan*-1-*one* p-*toluenesulphonylhydrazone*

(a) NaH (250 mg, 8.33 mmol) was added to a soln of the tosylhydrazone **43** (2.02 g, 6.16 mmol) in diglyme (50 ml). The mixture was stirred under N_2 overnight, and then heated in an oil bath at 180° for 45 min. The mixture was cooled, filtered, diluted with H_2O and worked up by ether extraction to give a brown oil (800 mg), homogeneous by glc (column B, 155°). Distillation gave 1,1a,6,6a-*tetrahydro*-6a-*methylcycloprop*[*a*]-*indene* **45** as a colourless oil (710 mg, 80%), b.p. 64°/0.1 mm. (Found: C, 91.7; H, 8.5. $C_{11}H_{12}$ requires: C, 91.6; H, 8.4%). NMR (CCl_4) δ: 7.28–6.78 (m, 4 H, ArH), 2.87 (s, 2 H, methylene), 1.94 (d of d, J 3.5, 8 Hz, 1 H, methine), 1.32 (s, 3 H, methyl), 0.84 (d of d, J 3.5, 3.5 Hz, 1 H, cyclopropane methylene). MS: 144 (M^+, 42%), 120 (100), 128 (39), 115 (16), 91 (5), 77 (5).

(b) NaH (85 mg, 2.8 mmol) was added to a soln of **43** (553 mg, 1.7 mmol) in THF (15 ml) under N_2. The mixture was stirred for 15 min, and then more THF (150 ml) was added, and the cooled mixture irradiated for 30 min. N_2 evolution ceased after 10 min (12 ml evolved, calc. vol = 37 ml). Evaporation of solvent, addn of H_2O and ether extraction gave a yellow solid (290 mg). Recrystallisation from aqueous EtOH gave 2,2-*dimethylindan*-1-*one azine* (50 mg, 10%) as bright yellow crystals, m.p. 123°. (Found: C, 83.3; H, 7.8. $C_{22}H_{24}N_2$ requires: C, 83.5; H, 7.7%). NMR (CCl_4) δ: 8.4 (m, 2 H, ArH), 7.17 (m, 6 H, ArH), 2.91 (s, 4 H, methylene), 1.42 (s, 12 H, methyl). MS (80°): 316 (M^+, 50%), 301 (20), 200 (10), 160 (23), 158 (30), 151 (16), 144 (100), 129 (25), 128 (23), 116 (50). Preparative tlc of the material from the mother liquors gave hydrocarbon **45** (20 mg, 9%), and more yellow material (790 mg), tentatively identified as a mixture of other stereoisomers of the azine (NMR).

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