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PHOTOCHEMICAL FORMAL [4π + 2π + 2π] CYCLOREVERSION OF 7,8-DIAZA-3-OXATRICYCLO[4.2.1.$0^{2,5}$]NON-7-ENES

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The photolysis and thermolysis of 7,8-diaza-3-oxatricyclo[4.2.1.$0^{2,5}$]non-7-enes were studied. Photolysis showed a novel [4π + 2π + 2π] cycloreversion in a formal way, the first example in azoalkane chemistry. This cycloreversion was found to be sensitized by the benzophenone produced. In contrast, thermolysis showed the typical decomposition pattern of azoalkanes, extrusion of nitrogen and subsequent σ-bond formation of the resulting biradical to afford the tricyclic oxetanes

INTRODUCTION

Denitrogenation of cyclic azoalkanes has attracted attention for decades as a unique synthetic tool for highly strained molecules[1] and polycyclic compounds,[2] and from mechanistic viewpoints.[3] Extrusions of nitrogen from bicyclic azoalkanes containing the 2,3-diazabicyclo[2.2.2]oct-2-ene skeleton by thermolysis or photolysis have been known to afford two major products, bicyclo[2.2.2]hexane and hexa-1,5-diene derivatives. These products were derived from a ring closure and a ring opening of the resulting biradicals, respectively.[4] A cyclobutane ring fusion at the 5- and 6-positions of these azoalkanes may create a new mode of denitrogenation in azoalkane chemistry, namely a formal [4π + 2π + 2π] cycloreversion. Scheme 1 summarizes the possible denitrogenation patterns of tricyclic azoalkanes **1** either by photolysis or thermolysis. In path *a*, the initially formed biradical **2** affords the cyclized product **3**. Extrusion of nitrogen in a [4π + 2π] cycloreversion[5] (path *b*) or cleavage of the σ-bond in biradical **2** (path *c*) results in the formation of diene **4**. A formal [4π + 2π + 2π] cycloreversion (path *d*) accompanied by the generation of ethylene hardly occurred, except in one example reported by Paquette and Leichter.[6] In their case, initially formed (**5**) from the corresponding azo compound either by photolysis or thermolysis at lower temperature was isolated and then thermolysed again at higher temperature to furnish a [σ2s + σ2s + σ2s] fragmentation. This reaction occurred only with a bridgehead phenyl substituent. However, to the best of our knowledge, there is no precedent for such a cycloreversion directly derived from azoalkanes.

As a continuation of our studies of novel rearrangements of biradicals,[7] we have designed this hitherto unknown formal [4π + 2π + 2π] cycloreversion in azoalkane chemistry. Our strategy is to create a tricyclic azoalkane similar to **1** in which the cyclobutane ring is replaced with an oxetane ring since a carbonyl formation from the corresponding biradical intermediate should be thermodynamically preferable to the formation of ethylene from **2**.

RESULTS AND DISCUSSION

Oxetane ring fused tricyclic azoalkanes **6** were prepared as follows. The *exo*-oxetanes[8] obtained from the photochemical [2π + 2π] cycloaddition between 2,3-dicarboethoxy-2,3-diazabicyclo[2.2.1]non-5-ene[9] and *p*-substituted benzophenones were hydrolysed (KOH–EtOH), decarboxylated and subsequently oxidized with $K_3Fe(CN)_6$.[10] The *exo* configuration of oxetane ring in **6** was confirmed from the 0–1 Hz vicinal coupling constants between the oxetane ring protons and the adjacent bridgehead protons.They showed n–π* absorption (λ_{max} 347 nm, ε_{max} 193 for **6a**; λ_{max} 347 nm, ε_{max} 163 for **6b**; and λ_{max} 347 nm, ε_{max} 194 for **6c**; EtOH as solvent) characteristic of a nitrogen–nitrogen double bond. Preparative photolysis of **6a** was carried out in benzene irradiated with a high-pressure mercury lamp through an aqueous $CuSO_4$ solution filter[11] under argon bubbling for 0·5 h. Three products, benzophenone (77%), *anti*-tricyclic oxetane **7a** (5%) and cyclopropanecarbaldehyde *cis*-**9a** (3%), were

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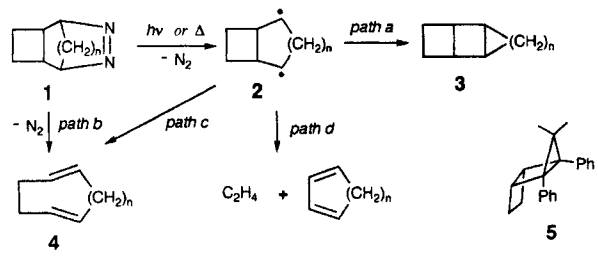
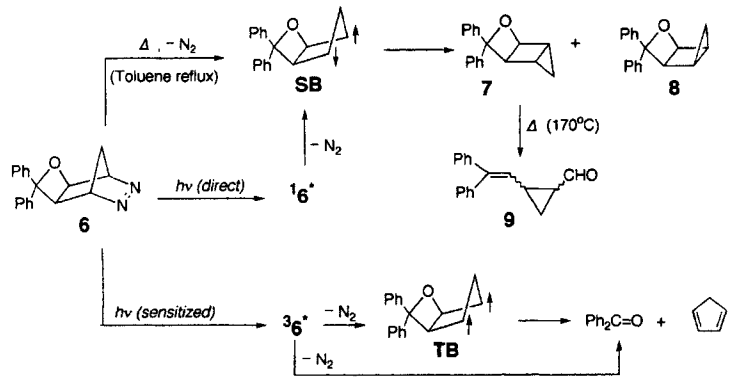


Scheme 1



Scheme 2

isolated by silica gel column chromatography. Photolysis of **6b** and **6c** afforded 4,4'-dichlorobenzophenone (70%) and 4,4'-dimethylbenzophenone (78%), respectively, accompanied by *cis*-**9b** (2%) in the case of **6b**. A control experiment showed that **7a** was stable under the photolytic conditions. Irradiation of the methanol solution of **6a** with a low-pressure mercury lamp did not lead to its denitrogenation, which showed that the excitation of the $n-\pi^*$ nitrogen–nitrogen double bond was really essential for this photolysis. *Anti* stereochemistry of **7a** was confirmed by its NOE difference spectrum. Ring junction protons, H_1 and H_5, showed an NOE relation with one of the geminal cyclopropane ring protons, $H_{3\beta}$. The other geminal proton, $H_{3\alpha}$, showed an NOE relation with two facing protons, H_2 and H_4 (see Figure 1). The ring skeleton of **7a**, a 6-oxatricyclo[3.2.0.$0^{2,4}$]heptane ring, has been reported once in literature, obtained from a secondary reaction in a photochemical reaction of 2,3-dihydrofuran.[12]

The progress of photolysis was monitored by ^{1}H NMR spectroscopy (270 MHz). Figure 2 shows that the product ratio depended on the irradiation time when the photolysis of **6a** ($9{\cdot}1 \times 10^{-2}$ M) was carried out in benzene-d_6 with a high-pressure mercury lamp through glass filters (340–380 nm). Cyclopentadiene was detected. As the photolysis progressed, the amount of cyclopentadiene gradually decreased owing to its benzophenone sensitized dimerization.[13] The ^{1}H NMR spectrum of the reaction mixture showed the formation of *syn*-tricyclic oxetane **8a**, the yield of which exceeded that of **7a**. An attempt to isolate **8a** by HPLC was unsuccessful. The cleavage of the oxetane ring in **8a** might be easily facilitated during separation to give *cis*-**9a**. Before the separation, an aldehyde proton signal

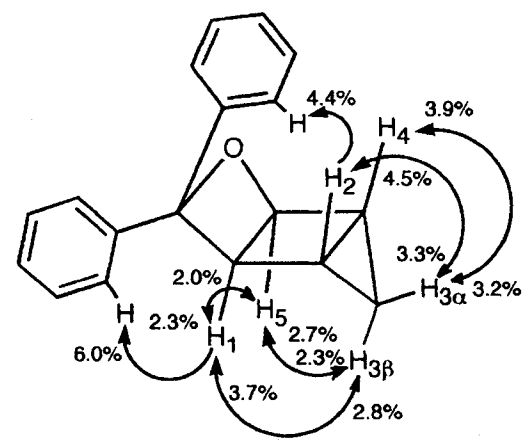


Figure 1. NOE relations in **7a**

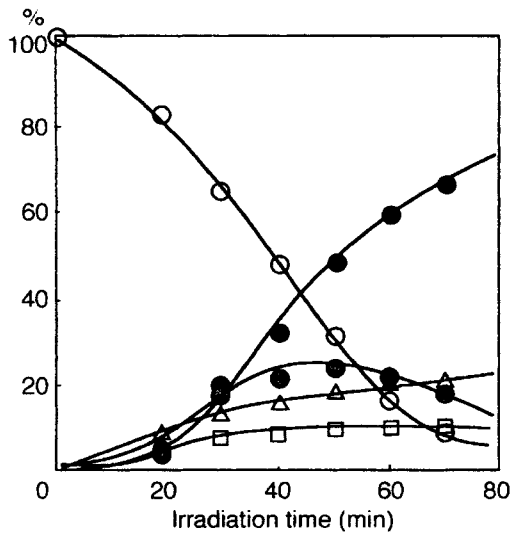


Figure 2. Progress of photolysis of **6a** in benzene-d_6 irradiated through glass filters ($\lambda = 340$–380 nm). (●) Benzophenone; (✹) Cyclopentadiene; (○) **6a**; (□) **7a**; (△) **8a**

was not detected in the irradiated sample by ^{1}H NMR spectroscopy. It seemed to require an induction period for the formation of benzophenone. This suggests the possibility of benzophenone-sensitized photolysis of **6a**. In proportion to the accumulation of benzophenone, the photolysis might be accelerated.

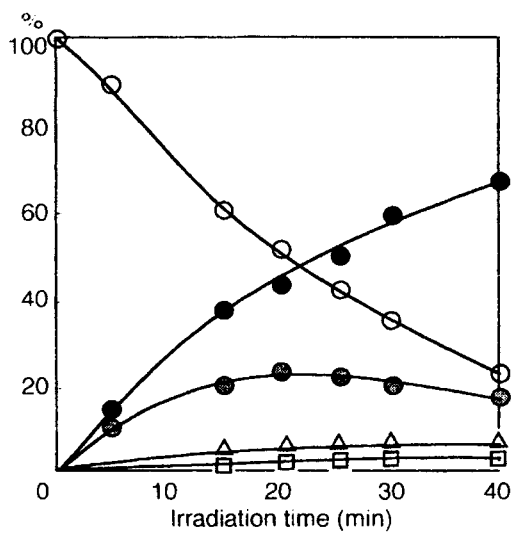


Figure 3. Progress of photolysis of **6a** in benzene-d_6 sensitized with benzophenone (0·65 equiv.), irradiated through glass filters ($\lambda = 340$–380 nm). (●) Benzophenone; (✹) cyclopentadiene; (○) **6a**; (□) **7a**; (△) **8a**

In order to establish that benzophenone produced in the photolysis was acting as a sensitizer, the photolysis of **6a** was carried out with 0·65 equiv. of benzophenone (see Figure 3). The amount of benzophenone produced was calculated by subtraction of the amount of benzophenone added from the total amount of benzophenone present in the reaction mixture. Noticeable acceleration of photolysis was observed from the very beginning and the total amount of **7a** and **8a** was suppressed.

The results indicate that mode of excitation, direct or sensitized, can switch the reaction paths. Figure 4 shows this phenomenon clearly. The product molar ratio, benzophenone/(**7a** + **8a**), is plotted against conversion (%) of the photolysis. The increase in this ratio at higher conversions suggests that benzophenone formed from the photolysis sensitizes the photolysis itself.

The effect of irradiation wavelength is interesting. Irradiation of **6a** with a high-pressure mercury lamp through an aqueous K_2CrO_4–Na_2CO_3 solution filter[8] resulted in the suppression of the benzophenone formation as shown in Figure 3. The molar absorption coefficients (ε) of **6a** and benzophenone in benzene are 2·6 and 18 at 366 nm and 67 and 67, respectively, at 313 nm. The larger ε value of **6a** at 313 nm than at 366 nm indicates that the direct excitation of n–π^* is more efficient at this wavelength than at 366 nm.

Since benzophenone produced in the photolysis sensitizes the reaction, the possible mechanism for the

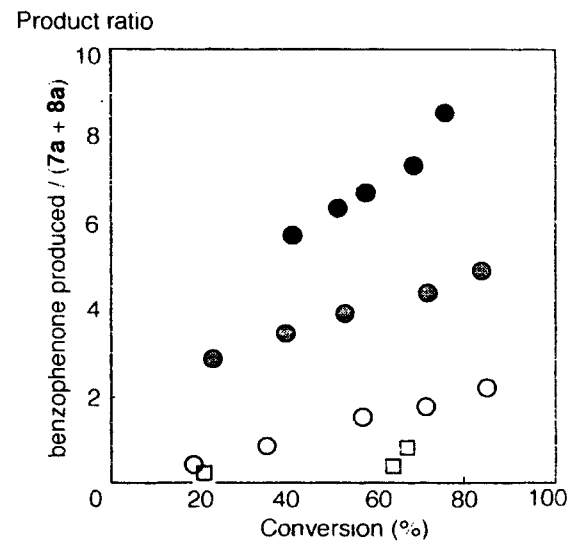


Figure 4. Plots of product ratio [benzophenone produced/(**7a** + **8a**) vs conversion of photolysis.. Irradiation through glass filters ($\lambda = 340$–380 nm); sensitized with (●) benzophenone (0·65 equiv.); (✹) with benzophenone (0·29 equiv.); (○) without benzophenone. (□) Irradiation through K_2CrO_4–Na_2CO_3 solution filter

formation of benzophenone is the involvement of the triplet biradical intermediate (**TB**). In contrast, the direct excitation of **2** results in the formation of the singlet biradical (**SB**), which subsequently creates a σ-bond between the two radical sites to give **7a** and **8a**.

It is important to note that some azoalkanes have different photochemical behaviour depending on their excited states.[4,14] In some cases, singlet excited azoalkanes result in the formation of nitrogen extruding products via diazenyl biradicals[15,16] and triplet excited azoalkanes afford aziranes via carbon–carbon bond cleavage. A similar cycloreversion involving a retro $4\pi+4\pi$ reaction of azoalkanes, fragmentation of a 1,3-radical cation, was recently reported by Adam and Sendelbach[17] using photosensistized electron transfer.

In contrast to photolysis, the thermolysis of **6a** in refluxing toluene for 3·5 h gave a totally different result, probably via **SB** exclusively. In this case, the formation of benzophenone (1%) was very suppressed, and instead **7a** (56%) was obtained as a major product together with *cis*-**9a** (6%) and recovered **6a** (3%) isolated by silica gel column chromatography. In a similar manner, **7b** was obtained from **6b** in 62% yield. In order to examine the generation of the biradical from **7a** via thermal ring opening of cyclopropane, **7a** was subjected to thermolysis at higher temperature. Unlike the reported thermolysis of **5**,[6] *cis*-**9a** (56%) and *trans*-**9a** (25%) were isolated when the benzene solution of **6a** was heated at 170 °C for 5 h in a sealed tube. Thermolysis of oxetanes has been known to afford carbonyl and olefin fragments.[18] In the present thermolysis, the oxetane ring was more labile than the cyclopropane ring.

The present findings show that the title azoalkanes have two modes of fragmentation depending on the method of denitrogenation.

EXPERIMENTAL

General methods. Melting points were determined on a Yanaco MP-S3 apparatus and are uncorrected. IR spectra were recorded on a Jasco A-202 spectrometer. UV spectra were measured with a Shimadzu UV-180 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on Jeol JNM-FX270, GSX-400, and GSX-500 spectrometers with TMS as an internal standard. Mass spectra were measured with a Hitachi RMU-7M mass spectrometer. Reaction solutions were concentrated on a rotary evaporator at 15–20 mmHg. Chromatographic separations were accomplished by flash column chromatography on silica gel (Fuji gel BW 200). Further purification of the reaction products was carried out by preparative HPLC with a LiChrosorb Si60 (Merck) column (7 μm; 250 × 10 mm i.d.) and *n*-hexane–ethyl acetate as eluent.

Preparation of tricyclic azoalkanes. To prepare 4,4-diphenyl-7,8-diaza-3-oxatricyclo[4.2.1.0^{2,5}]non-7-ene (**6a**), the $2\pi+2\pi$ adduct (0·546 g, 1·29 mmol) obtained from the photocycloaddition of diethyl 2,3-diazabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate and benzophenone was heated under reflux for 3 h in EtOH (20 cm^3) with KOH (1·587 g, 28·3 mmol). The resulting mixture was cooled to 0 °C and then aqueous $K_3Fe(CN)_6$ (1·310 g, 3·98 mmol) solution was added dropwise. After stirring for 3 h at 0 °C, the product was extracted with diethyl ether (100 cm^3 × 3) and dried over anhydrous $MgSO_4$. After evaporation of solvent, the residue was chromatographed on silica gel with benzene–ethyl acetate (13:1) to give **6a** (0·326 g, 91%) as colourless crystals, m.p. 135 °C (*n*-hexane–benzene); UV (EtOH), λ_{max} 224 nm (ε_{max} 9200), λ_{max} 347 nm (ε_{max} 193); ^{1}H NMR ($CDCl_3$, 500MHz), δ 7·50–7·08 (m, 10H), 5·58 (s, 1H), 5·46 (s, 1H), 4·57 (d, J = 5·0 Hz, 1H), 2·90 (d, J = 5·0 Hz, 1H), 1·77 (d, J = 12·0 Hz, 1H), 1·15 (d, J = 12·0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100MHz), δ 146·20 (s), 142·30 (s), 128·58 (d), 128·48 (d), 127·27 (d), 127·08 (d), 124·37 (d), 124·09 (d), 86·30 (s), 80·36 (d), 78·13 (d), 74·34 (d), 43·56 (d), 34·79 (t); MS [m/z with relative intensity (%) in parentheses], 248 ($M^+ - N_2$, 2), 204 (34), 192 (32), 191 (33), 183 (80), 165 (27), 115 (22), 105 (100), 91 (33). Analysis: calculated for $C_{18}H_{16}N_2O$, C 78·23, H 5·84, N 10·14; found, C 78·06, H 5·89, N, 10·05 %.

In a similar manner, 4,4-bis(4′-chlorophenyl)-7,8-diaza-3-oxatricyclo[4.2.1.0^{2,5}]non-7-ene (**6b**) and 4,4-bis(4′-methylphenyl)-7,8-diaza-3-oxatricyclo[4.2.1.0^{2,5}]non-7-ene (**6c**) were prepared in 82% and 61% yields, respectively. **6b**: colourless crystals, m.p. 127–128·5 °C (*n*-hexane–benzene); UV (EtOH), λ_{max} 232 nm (ε_{max} 17 500), λ_{max} 347nm (ε_{max} 163); ^{1}H NMR ($CDCl_3$, 500 MHz), δ 7·44–7·20 (m, 8H), 5·58 (s, 1H), 5·42 (s, 1H), 4·54 (dd, J = 5·2, 1·1 Hz, 1H), 2·71 (dt, J = 5·2, 1·4 Hz, 1H), 1·79 (d, J = 11·7 Hz, 1H), 1·14 (d, J = 11·7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 67·8 MHz), δ 144·29 (s), 140·46 (s), 133·52 (s), 133·34 (s), 128·94 (d), 128·91 (d), 125·8 (d), 125·80 (d), 125·47 (d), 85·56 (s), 80·21 (d), 77·82 (d), 74·44 (d), 43·41 (d), 34·73 (t); HRMS, m/z calculated for $C_{18}H_{14}Cl_2O$ ($M^+ - N_2$) 316·0421, found 316·0431. Analysis calculated for $C_{18}H_{14}Cl_2N_2O$, C 62·62, H 4·09, N 8·11; found, C 62·64, H 4·15, N 8·07%. **6c**: colourless crystals, m.p. 128–130 °C (*n*-hexane–benzene); UV (EtOH), λ_{max} 228 nm (ε_{max} 11 800), λ_{max} 347 nm (ε_{max} 194); ^{1}H NMR ($CDCl_3$, 500 MHz), δ 7·37–7·12 (m, 8H), 5·57 (s, 1H), 5·45 (s, 1H), 4·57 (dd, J = 5·0, 1·3 Hz, 1H), 2·77 (dt, J = 5·2, 1·3 Hz, 1H), 2·32 (s, 3H), 2·30 (s, 3H), 1·91 (d, J = 11·0 Hz, 1H), 1·12 (d, J = 11·0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 67·8 MHz), δ 143·60 (s), 139·51 (s), 136·93 (s), 136·61 (s), 129·23 (d), 129·14 (d), 124·27 (d), 123·93 (d), 86·35 (s), 80·40 (d), 78·21 (d), 74·30 (d), 43·41 (d), 34·87 (t), 21·07 (q), 20·96 (q); MS [m/z with relative intensity (%) in parentheses], 304 (M^+, 0·5), 276 (16), 247

(33), 232 (27), 219 (25), 211 (33), 155 (19), 119 (100). Analysis calculated for $C_{20}H_{20}N_2O$, C 78·92, H 6·62, N 9·20; found, C 78·91, H 6·70, N 9·17%.

Photolysis. Preparative photolysis of **6** (0·5–0·6 mmol) was performed in a Pyrex test-tube with benzene (10 cm^3) as a solvent under bubbling of argon with a 450 W high-pressure mercury lamp (Ushio UM-452) through an aqueous $CuSO_4$ solution filter ($CuSO4{\cdot}5H_2O$, 250 $g\,l^{-1}$, thickness 1 cm).[11]

A ^1H NMR (270 MHz) study of the photolysis of **6a** ($9{\cdot}1 \times 10^{-2}$ M) was carried out in an NMR tube with benzene-d_6 as a solvent. Prior to photolysis, the sample solution was purged by bubbling argon for 15 min. Irradiation was carried out through either glass filters ($\lambda = 340$–380 nm; Toshiba UV-35 + UV-D36A) or a solution filter (K_2CrO_4, 0·27 $g\,l^{-1}$ + Na_2CO_3, 1·0 $g\,l^{-1}$, thickness 1 cm)[11]. After the irradiation, ^1H NMR spectra of the resulting reaction mixture was immediately recorded and the product ratio was determined on integration.

Thermolyis. Thermolysis of **6** (0·40 mmol) was performed in refluxing toluene (20 cm^3) for 3·5 h. Thermolysis of **7a** (0·35 mmol) was carried out in benzene (7 cm^3) for 5 h at 170 °C in a sealed tube.

Photolysis and thermolysis products. anti-7,7-Diphenyl-6-oxatricyclo[3.2.0.$0^{2,4}$]heptane (**7a**); mp. 86 °C (*n*-hexane–benzene); ^1H NMR ($CDCl_3$, 500 MHz), δ 7·50–7·20 (m, 10H), 4·80 (dd, $J = 4{\cdot}1$, 2·6 Hz, 1H), 3·33 (t, $J = 2{\cdot}6$ Hz, 1H), 2·13 (m), 1·65 (ddd, $J = 5{\cdot}0$, 2·6, 1·1 Hz, 1H), 0·84 (q, $J = 5{\cdot}0$ Hz, 1H), 0·45 (dt, $J = 5{\cdot}0$, 1·1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz), δ 146·78 (s), 144·30 (s), 128·26 (d), 127·83 (d), 126·99 (d), 126·45 (d), 125·39 (d), 125·32 (d), 89·21 (s), 80·07 (d), 50·57 (d), 22·89 (d), 16·52 (d), 9·50 (t); MS [*m/z* with relative intensity (%) in parentheses], 248 (M^+, 4), 219 (19), 183 (69), 165 (21), 115 (21), 105 (44), 91 (54), 66 (100). Analysis calculated for $C_{18}H_{16}O$, C 87·06, H 6·50; found, C 87·16, H 6·58%. *syn*-7,7-Diphenyl-6-oxatricyclo[3.2.0.$0^{2,4}$]heptane (**8a**): ^1H NMR ($CDCl_3$, 400 MHz) spectrum of **8a** (except phenyl group) deduced from the reaction mixture, δ 4·95 (dt, $J = 6{\cdot}4$, 2·5 Hz, 1H), 3·29 (dd, $J = 6{\cdot}4$, 4·2 Hz, 1H), 2·22 (m, 1H), 2·14 (m, 1H), 1·74 (dt, $J = 5{\cdot}0$, 1·2 Hz, 1H), 0·68 (dt, $J = 6{\cdot}4$, 5·0 Hz, 1H). *anti*-7,7-Bis(4′-chlorophenyl)-6-oxatricyclo[3.2.0.$0^{2,4}$]heptane (**7b**): colourless oil; ^1H NMR ($CDCl_3$, 500 MHz), δ 7·7–7·28 (m, 8H), 4·75 (dd, $J = 4{\cdot}4$, 2·2 Hz, 1H), 3·26 (t, $J = 2{\cdot}4$ Hz, 1H), 2·12 (m, 1H), 1·59 (m, 1H), 0·86 (q, $J = 5{\cdot}5$ Hz, 1H), 0·45 (d, $J = 5{\cdot}5$, 1·2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125·7 MHz), δ 144·79 (s), 142·42 (s), 133·12 (s), 132·64 (s), 128·54 (d), 128·16 (d), 126·81 (d), 88·36 (s), 80·14 (d), 50·34 (d), 22·98 (d), 16·42 (d), 9·47 (t); HRMS, *m/z* calculated for $C_{18}H_{14}Cl_2O$ (M^+) 316·0420, found 316·0415. *cis*-2-(2′,2′-Diphenyl)ethenyl-1-cyclopropanecarbaldehyde (*cis*-**9a**): colourless oil; IR ($CHCl_3$), 1700 cm^{-1} (C=O) ^1H NMR ($CDCl_3$, 500 MHz), δ 9·51 (d, $J = 5{\cdot}9$ Hz, 1H), 7·41–7·16 (m, 10H), 5·98 (d, $J = 9{\cdot}5$ Hz, 1H), 2·25 (dtd, $J = 9{\cdot}5$, 8·0, 6·0 Hz, 1H), 2·16 (tdd, $J = 8{\cdot}0$, 6·0, 5·9 Hz, 1H), 1·62 (dt, $J = 7{\cdot}0$, 6·0 Hz, 1H), 1·45 (td, $J = 8{\cdot}0$, 7·0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz), δ 200·53 (d), 144·43 (s), 141·94 (s), 139·61 (s), 130·09 (d), 128·35 (d), 128·29 (d), 128·17 (d), 127·38 (d), 127·34 (d), 125·29 (d), 31·62 (d), 25·20 (d), 16·85 (t); HRMS [electron impact (EI)], calculated for $C_{18}H_{16}O$ (M^+) 248·1200, found 248·1198. *trans*-2-(2′,2′-Diphenyl)ethenyl-1-cyclopropanecarbaldehyde (*trans*-**9a**): colourless oil; IR ($CHCl_3$) 1695 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, 500 MHz), δ 9·02 (d, $J = 5{\cdot}3$ Hz, 1H), 7·41–7·17 (m, 10H), 5·46 (d, $J = 9{\cdot}7$ Hz, 1H), 2·23 (dddd, $J = 9{\cdot}7$, 9·0, 6·3, 3·7 Hz, 1H), 2·05 (dddd, $J = 8{\cdot}4$, 5·3, 4·9, 3·7 Hz, 1H), 1·58 (dt, $J = 9{\cdot}0$, 4·9 Hz, 1H), 1·31 (ddd, $J = 8{\cdot}4$, 6·3, 4·9 Hz, 1H); HRMS (EI), calculated for $C_{18}H_{16}O$ (M^+) 248·1200, found 248·1201.

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