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Realization of Photo-Thermal Metathesis Under Microwave Irradiation Conditions: An Entry to Triquinane Frameworks

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Abstract: We report a simple and convenient synthetic route to *cis,syn,cis* triquinane frameworks under microwave irradiation conditions starting with cage diones. This is feasible because of the substituents present in the precursors, which facilitate the metathesis under milder reaction conditions as compared to normal flash vacuum pyrolysis conditions (~ 600 °C). Isomerization of the double bond was realized under microwave irradiation to deliver the other triquinanes, which are useful precursors for natural product synthesis.

Introduction

Chemistry of cage compounds (e.g. Cookson's dione **1**) has been expanded during the last few decades.[1] Due to various applications of these compounds in diverse areas of chemistry such as synthesis of natural products,[2] medicinal chemistry, and high energy materials,[3] there is a pressing need to develop new strategies for their assembly. Synthesis of these molecules has become a worthwhile objective due to rigid structures associated with their compact skeletons.[4]

Triquinane[5] natural products containing linearly as well as angularly fused frameworks gained considerable interest due to their biological activity.[6] After isolation of the hirsutic acid-C in 1966, several triquinane natural products have been isolated from plant, marine and microbial sources.[7a] Recently, published article indicate that 118 linear triquinane based sesquiterpenes were isolated and identified.[7b] Therefore, new methods to assemble linear triquinanes is worthy of further investigation. These products exhibit interesting biological activities. For example, hirsutic acid has antibiotic properties, coriolin shows antibacterial and antitumor activities, while capnellene (**2**) (Figure 1) and its analogs act as chemical defense agents and they inhibit the growth of microorganisms and also prevent larval settlement.

Triquinane framework with *cis-anti-cis* configuration is a key structural element present in several cyclopentanoid natural products. Their biological activity and stereochemical intricacies justify thier synthesis.[8] In this context, capnellene (**2**),[9] (+)-connatusin (**3**),[10] (−)-complicatic acid (**4**),[11] ceratopicanol (**5**),[12] cucumin E (**6**),[13] hypnophilin (**7**)[14] (Figure 1) represent selected synthetic targets. Several groups are engaged in design and synthesis of quinane-based targets. To this end, Shono and co-workers[15] have employed a sequential electro

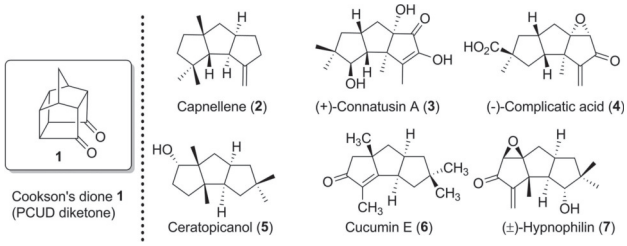

Figure 1. Biologically active triquinane derivatives.

reductive cyclization as a key step for the generation of the triquinane moiety, which represents the formal synthesis of (±)-capnellene (**2**). In another instance, Oda and co-workers[16] designed a five-step synthetic sequence to construct the hirsutene natural product. West and co-workers[17a] utilized [4+4] photocycloaddition and thermal decarboxylation sequence for assembling the decorated triquinanes. Due to space limitation, it is not possible to describe various interesting strategies reported in the literature.[17b–m]

In this context, photo-thermal metathesis was found to be a valuable tool to construct triquinane frameworks suitable for natural product synthesis. Mehta and co-workers demonstrated a step-wise photo-thermal olefin metathesis to design triquinane frames[18] involving thermal activation of pentacycloundecane dione (PCUD) systems. Interestingly, PCUD has been converted into *cis,syn,cis* linear triquinane via regiospecific thermal fragmentation of the cyclobutane ring. For this purpose, flash vacuum pyrolysis (FVP) conditions at high temperature (600–700 °C) has been used. This strategy was further extended to the synthesis of various natural products such as hirsutene, coriolin, and $\Delta^{7(10)}$-capnellene (**2**),[19] precapnelladiene,[20] and ikarugamycin ring system.[21]

Generally, FVP technique is used for thermolysis of the strained cyclobutane ring present in the PCUD systems.[22a] Alternatively, Mehta and co-workers also developed acid catalyzed transformation to triquinane ring systems starting with a suitable derivatives of Cookson's dione.[22b] This ring fragmentation in PCUDs is facile, when the electron-donating substituents are present at C-1 or/and C-7 position of Cookson's

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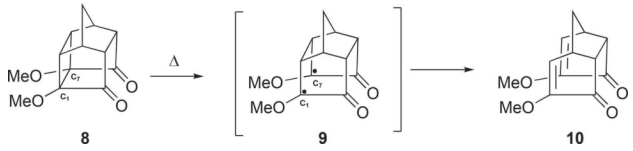
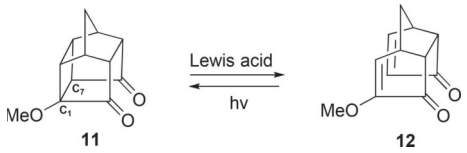
dione. In addition, Kanematsu and co-workers[23] reported that the presence of 1,7-dimethoxy groups in the Cookson's dione **8**, increaeses the C_1–C_7 bond length due to synergistic captodative stabilization of 1,4-diradical such as **9**. It is interesting to note that the methoxy group stabilizes the carbon radical by 4 to 5 kcal/mol in contrast to methyl group. When two methoxy groups were attached to C_1–C_7 bond, better activation was expected. Hence, the dimethoxy substituted Cookson's dione **8** showed an unusual reactivity towards the formation of triquinane molecule **10** (Scheme 1). Thus, the 1,7-dimethoxy containing cage dione **8** underwent cycloreversion in refluxing benzene. On the contrary, 1-methoxy-substituted cage system (*e.g.,* **11**) did not give cycloreversion. It was quite stable under these conditions. Interestingly, a cycloreversion of 1-methoxy-substituted cage compound **11** was realized under Lewis acid conditions to give triquinane derivative **12** (Scheme 2).[2c]

Electron-donating substituents provided a push-pull mechanism and synergistic captodative stabilization in PCUD systems. In view of these aspects, we have studied the X-ray crystallographic data of several substituted cage compounds and found that the presence of substituents influench the C_1–C_7 bond length. So, we investigate the photo-thermal metathesis under MWI conditions. To this end, various PCUD systems were separately subjected to the photo-thermal metathesis under microwave irradiation (MWI) conditions (150 W, 180–240 °C) to provide the respective linear triquinane derivatives.



Scheme 1. A captodative stabilization of 1,4-diradical in Cookson's dione **8**.



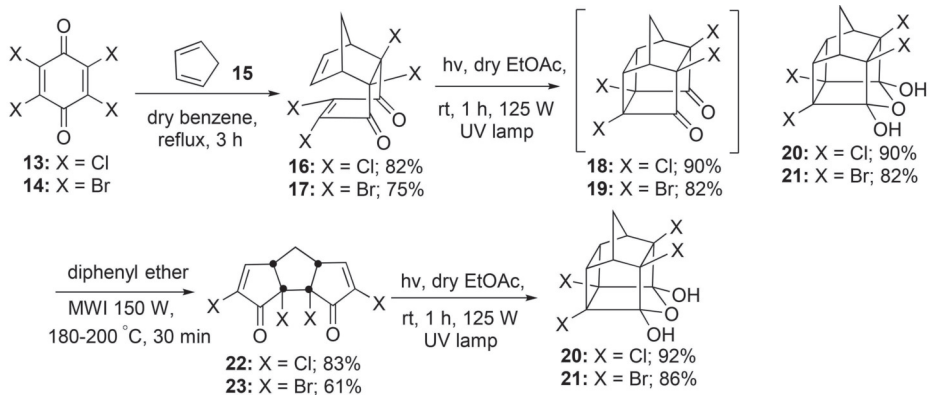
Scheme 2. Cycloreversion of 1-methoxy-substituted cage compound **11**.

Results and Discussion

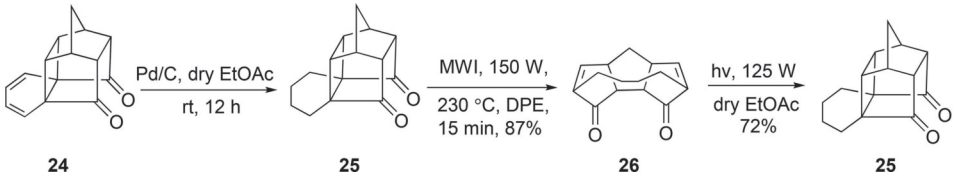
Substituted PCUDs gained considerable attention because of their ease of conversion to triquinane skeleton via FVP conditions. The new tactics involving MWI conditions for the synthesis of triquinanes, provide an alternate route to various triquinane-based natural products. To test MWI conditions, the required PCUD derivatives were prepared via the Diels-Alder reaction and [2+2] photocycloaddition sequence staring with a readily accessible starting materials such as 1,3-cyclopentadiene and *p*-benzoquinone derivatives.

Various PCUDs were prepared by following the known procedures and studied their [2+2] cycloreversion sequence. The cycloadducts **16** and **17**[2a,18] were assembled via a Diels-Alder reaction of halo benzoquinones such as **13** and **14** with cyclopentadiene (**15**). Later, these compounds **16** and **17** were subjected to [2+2] photocycloaddition with the aid of 125 W mercury vapor lamp in a quartz immersion vessel by using pyrex filter to generate the respective cage compounds **20** and **21**.[2a,18] The expected diones **18** and **19** were not isolated due to their facile hydration tendency and the hemiacetals **20** and **21** were isolated. Later, these cycloaddition products *e.g.,* **20** and **21** were subjected to a photo-thermal metathesis under MWI conditions using diphenyl ether (DPE) as a solvent. Here, DPE is a prefered solvent due its high boiling point. These conditions led to the formation of the corresponding tetra-halo-triquinanes **22** and **23**.[2a] Finally, [2+2] photocycloaddition of triquinanes **22** and **23** in dry ethyl acetate furnished the products **20** and **21** (Scheme 3), which proved the stereochemistry of ring opened products as *cis,syn,cis* stereochemistry.

Further, this strategy can be extended to the synthesis of substituted triquinane **26** (Scheme 4).[24] The hexacyclic-caged compound **25** can be derived from **24** by hydrogenation sequence. The PCUD system **25** is a suitable substrate for photo-thermal metathesis, which was subjected to MWI conditions in DPE to afford a tricyclic dione **26**. Next, the compound **26** was subjected to [2+2] photocycloaddition in the presence of 125 W mercury vapor lamp in a quartz immersion vessel using a pyrex filter furnished the cage compound **25**. This observation distinctly shows the stereochemistry of **26** is *cis,syn,cis* (Table 1 & 2).

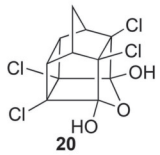
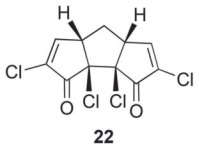
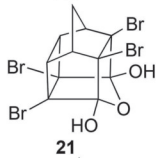
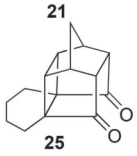
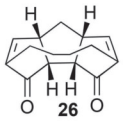
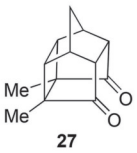
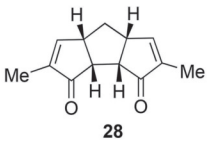
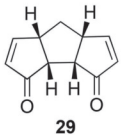


Scheme 3. Synthesis of halo substituted PCUD derivatives.



Scheme 4. Synthesis of cyclohexane substituted PCUD derivatives.

Table 1. Photo-thermal metathesis of cage systems **1**, **20**, **21**, **25**, and **27** under conventional heating (oil bath) and FVP conditions.[2a,24]

S. No	Caged molecules	Triquinanes	[a]Temp (°C)	Time (min)	Yields(%)
1.	 **20**	 **22**	240 °C/A	30 min	95
2.	 **21**	 **23**	260 °C/A	10 min	70
3.	 **25**	 **26**	550°C/B (1 torr)	-------	70
4.	 **27**	 **28**	450°C/B 260°C/A	------- 30 min	100 20
5.	 **1**	 **29**	560 °C/B (1 torr)	------	96

A = Conventional heating in diphenyl ether (DPE) solvent
B = Flash vacuum pyrolysis (FVP) conditions

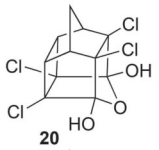
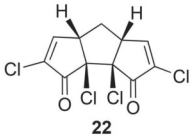
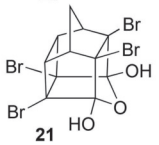
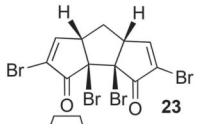
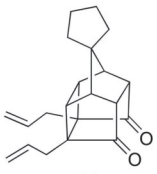
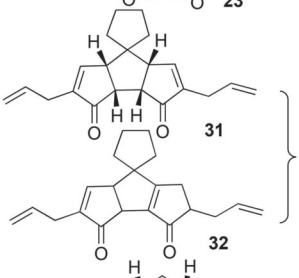
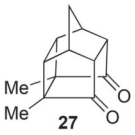
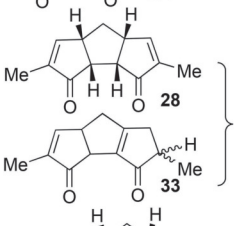
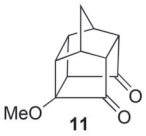
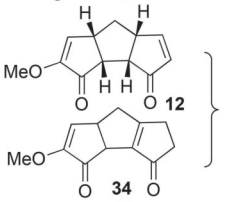
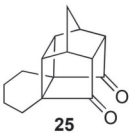
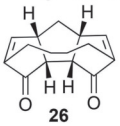
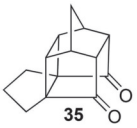
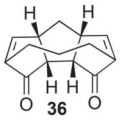
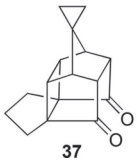
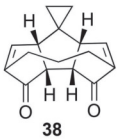
Similarly, the pentacyclic adduct **27** (Table 2) was subjected to the photo-thermal metathesis under MWI conditions (150 W, 240 °C, 40 min) using DPE as a solvent to produce the dimethyl triquinane derivative **28** (57%) along with double bond isomerized triquinane **33** in 15% yield (shown in Table 2). Photocyclization of compound **28** in 125 W mercury vapor lamp in a quartz immersion vessel using pyrex filter in dry ethyl acetate delivered the cage compound **27**, which indicates the *cis,syn,cis* nature of tricyclic dione **28** (Table 2). Later, the cage dione **11** was subjected to photo-thermal metathesis under similar reaction conditions (MWI, 150 W, 200 °C) to deliver a mixture of products **12** and **34** in good yields (Table 2).

Similarly, diallyl spiro cage dione **30**[25] was subjected to the photo-thermal metathesis under MWI conditions (150 W, 220 °C, 30 min) in DPE produced the corresponding diallyl triquinane derivative **31** (29%) along with a double bond isomerized product **32** in 47% yield (Table 2).

Additionally, we studied two new examples of cage diones **35** and **37** which were not reported by FVP method (Table 2). In this context, the cage diones **35** and **37**[26,27] containing fused five membered rings had undergone photo-thermal metathesis sequence under MWI conditions (150 W, 230 °C, 20 min/DPE) to generate the respective triqunanes **36** (62%) and **38** (58%). Unfortunately, the parent dione **1** failed to give ring-opened product **29** under MWI conditions. This observation clearly indicate that the substituents present in cyclobutane ring provide the necessery driving force for the cleavage of strained ring. Triquinane **29** was realized only under FVP conditions at high temperature (600 °C).

The structure of the triquinane derivatives were established based on ^{1}H NMR and ^{13}C NMR spectral data and their data matched with the reported values. In addition, the structures of isomerized product **34** and triquinane derivative **38** were confirmed by single-crystal X-ray diffraction studies (Figure 2).[27]

Table 2. Photo-thermal metathesis of cage systems under MWI conditions.

S. No	Caged molecules	Triquinanes	Temp (°C)/Watt	Time (min)	Yields(%)
1.	 **20**	 **22**	200 °C/150 W	30 min	83
2.	 **21**	 **23**	180 °C/150 W	20 min	61
3.	 **30**	 **31** **32**	220°C/150 W	30 min	29 47
4.	 **27**	 **28** **33**	240°C/150 W	40 min	57 15
5.	 **11**	 **12** **34**	200°C/150 W	20 min	22 59
6.	 **25**	 **26**	230°C/150 W	15 min	87
7.	 **35**	 **36**	230°C/150 W	20 min	62
8.	 **37**	 **38**	230°C/150 W	20 min	58

Previous (Conventional Heating) and Present (MWI) Studies

Mehta and co-workers reported[2a,18,24] various triquinanes such as **26**, **28**, and **29** from cage dione systems **1**, **25**, and **27** illustrated in Table 1 under very high temperature conditions (~ 600 °C) which require special equipment. They also reported chloro and bromo derived triquinanes **22** and **23** from hydroxy cage compounds **20** and **21** via conventional oil bath heating at 240–260 °C in DPE solvent.

The compounds prepared under MW irradiation has advantageous due to ease of operation and mild conditions tolerate sensitive substrates as compared with the FVP conditions. Interestingly, the double bond isomerized triquinanes **32**, **33**, and **34** was also realized under MWI condition with methoxy, methyl and allyl substituted cage compounds such as **11**, **27**, and **30**. (Table 2). We did not observe isomerization of double bond after metathesis of fused ring cage systems such as **25**, **35**, and **37**.

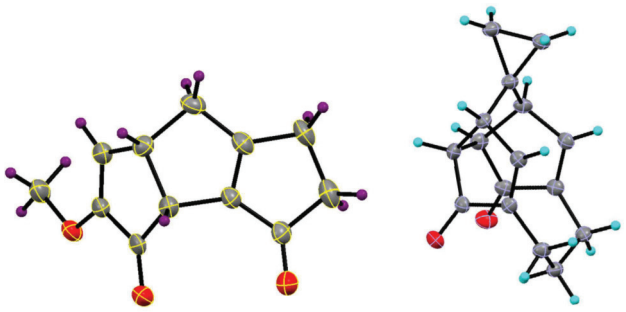


Figure 2. X-ray crystal structures of triquinanes **34** and **38**.

Conclusion

We have demonstrated a simple and an alternate way to FVP protocol to synthesize triquinane frameworks under MW irradiation conditions starting with substituted PCUD derivatives. Interestingly, the substitutents present in the cage systems prompted the cleavage of C–C bond under MWI conditions. These conditions provide an alternate tactics to generate *cis,syn,cis* triquinane frameworks, which may useful to design natural and unnatural products containing cyclopentanoids. We have also reported four new examples of triquinanes **31**, **32**, **36**, and **38** under MWI conditions from cage diones **30**, **35**, and **37** which were not reported earlier. Also, we isolated double bond isomerized triquinanes **32**, **33**, and **34** under these conditions and these are useful synthons in total synthesis of natural products.

Experimental Section

General Experimental Details/Methods

Reagents, chemicals, materials, and required solvents were obtained from the commercial sources and used as such without any further purification. Analytical TLC was performed on (10×5) glass plates coated with Acme's silica gel (GF-254) containing 13% calcium sulfate as a binder. Progress of the reactions were monitored by TLC using suitable solvent system and visualization was done under UV light, exposure to iodine vapour and by immersion into a solution of $KMnO_4$. Anhydrous reactions (air, moisture sensitive) were performed in oven-dried glassware under argon/nitrogen atmosphere by using standard syringe-septum techniques. Acme's silica gel (100–200 mesh size) was used for column chromatography and solvents were evaporated under vacuo on rotary evaporator. Benzene and DCM was distilled from CaH_2 and ethyl acetate was dried over K_2CO_3.

Infra-red spectra had been recorded on a Nicolet Impact-400 FTIR spectrometer and samples were prepared as a thin film between CsCl plates by dissolving the compound in CH_2Cl_2 and $CHCl_3$ and then evaporating the solvent. ^{1}H NMR (400 and 500 MHz), ^{13}C NMR, ^{13}C-APT NMR, DEPT 135 NMR (100 and 125 MHz) spectra were recorded on Bruker spectrometer and samples were prepared in $CDCl_3$ solvent. The chemical shifts are reported in parts per million (ppm) on delta scale with TMS as an internal standard. The values for the coupling constants (*J*) are given in Hz. The abbreviations for ^{1}H NMR spin couplings are given as s, d, t, q, dd, dt, td, and m for singlet, doublet, triplet, quartet, doublet of doublet, doublet of triplet, triplet of doublet and multiplet, respectively. High-resolution mass spectra (HRMS) for all the compounds were recorded in a positive ion electrospray ionization (ESI, Q-TOF). Melting points were recorded on veego VMP-CMP melting point apparatus and are uncorrected. All reported yields are isolated yields of the products after column purification. Single-crystal X-ray diffraction analysis was performed on diffractometer equipped with graphite monochromated Mo Kα radiation and structure was solved by direct methods shelxl-97 and refined by full-matrix least-squares against F^2 using shelxl-97 software. Microwave irradiation (MWI) was carried out with commercially available microwave reactor such as CEM Discover-sp, CEM Corporation, North Carolina, USA and the reaction temperature was maintained by an external infrared sensor.

General Procedures and Characterisation Data for All (Known/New) Compounds

General Experimental Procedure for Photo-Thermal Metathesis under Microwave Irradiation (MWI) Conditions

The cage hemiketals **20**–**21** (0.39–0.75 mmol) and cage diones **11**, **25**, **27**, **30**, **35**, and **37** (0.20–0.49 mmol) was dissolved in minimum volume of diphenyl ether (3–5 mL) and subjected to microwave irradiation (150 W) at 180–240 °C for 15–40 min using CEM Sp instrument. At the conclusion of the reaction (TLC monitoring), the crude triquinane derivatives were purified by column chromatography using appropriate mixture of ethyl acetate in petroleum ether to obtain respective triquinane derivatives **12**, **22**, **23**, **26**, **28**, **31**, **32**, **33**, **34**, **36**, and **38** in moderate to good yields.

Triquinane 12[2c]

Prepared according to the above general procedure using cage dione **11** (100 mg, 0.48 mmol) and diphenyl ether (3 mL) under MWI for 20 min. Column chromatography (50% ethyl acetate in petroleum ether) afforded the pure crystalline triquinane **12**. Colourless solid; Yield: 22 mg (22%); mp: 110–112 °C; (lit. reported[2c] mp: 107 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.46 (dd, *J* = 5.5, 2.3 Hz, 1H), 6.10 (d, *J* = 2.7 Hz, 1H), 5.90 (dd, *J* = 5.4, 1.9 Hz,1H), 3.61 (s, 3H), 3.53–3.50 (m, 1H), 3.38–3.35 (m, 1H), 3.27–3.19 (m, 2H), 2.26 (td, *J* = 14.0, 9.8 Hz, 1H), 1.83 (d, *J* = 14.2 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 207.2, 200.1, 166.5, 156.3, 133.1, 128.8, 57.2, 53.6, 52.2, 50.6, 43.9, 32.9 ppm; HRMS (ESI): *m/z* calcd for $C_{12}H_{12}NaO_2$ $[M+Na]^+$: 227.0679; found: 227.0679.

Triquinane 34

Prepared according to the above general procedure using cage dione **11** (100 mg, 0.48 mmol) and diphenyl ether (3 mL) under MWI for 20 min. Column chromatography (70% ethyl acetate in petroleum ether) afforded the pure crystalline isomerized triquinane **34**. Colourless crystalline solid; Yield: 59 mg (59%); mp: 153–155 °C; IR (neat, cm^{-1}): 2938, 2925, 2840, 1720, 1690, 1623, 1457, 1444, 1425, 1373, 1347, 1322, 1281, 1258, 1215, 1190, 1153, 1110, 1047, 1029, 988, 954, 915, 875, 839, 785, 699, 612; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.28 (d, *J* = 3.18 Hz, 1H), 3.90–3.86 (m, 1H), 3.69 (s, 3H), 3.61–3.58 (m, 1H), 2.95–2.88 (m, 1H), 2.68 (t, *J* = 4.5 Hz, 2H), 2.49–2.39 (m, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 201.5, 197.7, 185.5, 156.0, 143.8, 127.9, 57.2, 49.7, 43.1, 40.6, 37.0, 25.9 ppm; HRMS (ESI): *m/z* calcd for $C_{12}H_{12}NaO_2$ $[M+Na]^+$: 227.0679; found: 227.0672. Selected X-ray data: $C_{12}H_{12}O_3$, M =

204.22, Monoclinic, Space group = C/c, Unit cell: a = 4.6057 (4) Å^3, b = 15.9079 (11) Å^3, c = 13.4376 (11) Å^3, α = 90°, β = 97.958 (8) °, γ = 90°, Z = 4, ρcald = 1.391 mg/m^3, F(000) = 432, λ = 0.71073 Å, μ = 0.100 mm^{-1}, Total/unique reflections = 7025/1717, Final *R* indices [*I* > 2sigma (*I*)]: R1 = 0.0535, ωR2 = 0.1103, *R* indices (all data): R1 = 0.0684, ωR2 = 0.1219.

Triquinane 22[2a,18]

Prepared according to the above general procedure using cage hemiketal **20** (250 mg, 0.75 mmol) and diphenyl ether (5 mL) under MWI for 30 min. Column chromatography (30% ethyl acetate in petroleum ether) afforded the pure crystalline triquinane **22**. Colourless crystalline solid; mp: 150–152 °C; (lit. reported[2a] mp: 149–150 °C); Yield: 197 mg (83%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (d, *J* = 2.8 Hz, 2H), 3.76 (dt, *J* = 10.1, 2.3 Hz, 2H), 2.87 (dt, *J* = 14.5, 10.1 Hz, 1H), 2.03 (dt, *J* = 14.5, 1.9 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 190.4, 154.2, 133.9, 76.8, 56.6, 30.5 ppm; HRMS (ESI): *m/z* calcd for $C_{11}H_6Cl_4KO_2$ $[M+K]^+$: 348.8753; found: 348.8752.

Triquinane 23[2a,18]

Prepared according to the above general procedure using cage hemiketal **21** (200 mg, 0.39 mmol) and diphenyl ether (5 mL) under MWI for 20 min. Column chromatography (25–30% ethyl acetate in petroleum ether) afforded the pure crystalline triquinane **23**. Colourless crystalline solid; Yield: 117 mg (61%); mp: 190–192 °C; (lit. reported[2a] mp: 196–198 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 2.9 Hz, 2H), 3.84 (dt, *J* = 10.3, 2.5 Hz, 2H), 2.86 (dt, *J* = 14.3, 10.2 Hz, 1H), 1.92 (dt, *J* = 14.4, 2.3 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 190.5 157.8, 123.3, 69.5, 59.3, 31.1 ppm; HRMS (ESI): *m/z* calcd for $C_{11}H_6Br_4KO_2$ $[M+Na]^+$: 508.6993; found: 508.6994.

Triquinane 26[24]

Prepared according to the above general procedure using cage dione **25** (100 mg, 0.43 mmol) and diphenyl ether (3 mL) under MWI for 15 min. Column chromatography (30% ethyl acetate in petroleum ether) afforded the pure crystalline triquinane **26**. Colourless crystalline solid; Yield: 87 mg (87%); mp: 161–163 °C; (lit. reported[24] mp: 158 °C);^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.88 (s, 2H), 3.40–3.34 (m, 4H), 2.27 (t, *J* = 11.7 Hz, 2H), 2.11–2.03 (m, 1H), 1.94–1.84 (m, 3H), 1.74–1.67 (m, 2H), 1.43–1.35 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 208.2, 160.3, 148.6, 55.8, 47.9, 32.1, 28.1, 25.7 ppm; HRMS (ESI): *m/z* calcd for $C_{15}H_{16}KO_2$ $[M+K]^+$: 267.0782; found: 267.0781.

Triquinane 28[2a,18]

Prepared according to the above general procedure using cage dione **27** (100 mg, 0.49 mmol) and diphenyl ether (3 mL) under MWI for 40 min. Column chromatography (30% ethyl acetate in petroleum ether) afforded the pure crystalline triquinane **28**. Colourless solid; Yield: 57 mg (57%); mp: 97–99 °C; (lit. reported[2a] mp: 93–94 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.99 (s, 2H), 3.36–3.33 (m, 2H), 3.26–3.24 (m, 2H), 2.21–2.12 (m, 1H), 1.80 (d, *J* = 13.9 Hz, 1H), 1.61 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 207.7, 159.4, 141.3, 53.8, 48.1, 31.9, 10.2 ppm; HRMS (ESI): *m/z* calcd for $C_{13}H_{14}NaO_2$ $[M+Na]^+$: 225.0886; found: 225.0884.

Triquinane 33[2a,18]

Prepared according to the above general procedure using cage dione **27** (100 mg, 0.49 mmol) and diphenyl ether (3 mL) under MWI for 40 min. Column chromatography (50% ethyl acetate in petroleum ether) afforded the pure crystalline triquinane **33**. Colourless solid; Yield: 15 mg (15%); mp: 115–117 °C; (lit. reported[2a] mp: 108–109 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.18 (s, 1H), 3.90 (brs, 1H), 3.60 (s, 1H), 2.88–2.68 (m, 3H), 2.41 (d, *J* = 18.8 Hz, 1H), 2.09 (d, *J* = 16.6 Hz, 1H), 1.75 (s, 3H), 1.20 (d, *J* = 6.6 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 205.3, 204.4, 182.6, 158.4, 143.4, 140.3, 51.1, 47.1, 46.5, 35.9, 34.7, 16.7, 10.5 ppm; HRMS (ESI): *m/z* calcd for $C_{13}H_{14}KO_2$ $[M+K]^+$: 241.0625; found: 241.0628.

Triquinane 36

Prepared according to the above general procedure using cage dione **35** (90 mg, 0.42 mmol) and diphenyl ether (3 mL) under MWI for 20 min. Column chromatography (30% ethyl acetate in petroleum ether) afforded the pure crystalline triquinane **36**. Colourless solid; Yield: 56 mg (62%); mp 146–148 °C; IR (neat, cm^{-1}): 2952, 2928, 2854, 1744, 1720, 1623, 1464, 1446, 1337, 1286, 1269, 1183, 1139, 1124,1063, 1024, 917, 853, 805, 776; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.70 (s, 2H), 3.50 (t, *J* = 2.3 Hz, 2H), 3.40 (d, *J* = 7.3 Hz, 2H), 2.56–2.52 (m, 2H), 2.46–2.39 (m, 2H), 2.18–1.98 (m, 2H), 1.88 (d, *J* = 13.8 Hz, 1H), 1.56–1.47 (m, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 208.5, 158.6, 148.8, 57.8, 48.1, 32.1, 25.9, 20.6 ppm; HRMS (ESI): *m/z* calcd for $C_{14}H_{14}KO_2$ $[M+K]^+$: 253.0625; found: 253.0626.

Triquinane 38

Prepared according to the above general procedure using spiro cage dione **37** (100 mg, 0.41 mmol) and diphenyl ether (3 mL) under MWI for 20 min. Column chromatography (25% ethyl acetate in petroleum ether) afforded the pure crystalline triquinane **38**. Colourless crystalline solid; Yield: 58 mg (58%); mp 187–189 °C; IR (neat, cm^{-1}): 2969, 2945, 2908, 2840, 1715, 1693, 1620, 1457, 1430, 1341, 1320, 1225, 1181, 1125, 1085, 1061, 1022, 937, 920, 898, 848, 807, 780; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.78 (s, 2H), 3.65 (t, *J* = 1.9 Hz, 2H), 2.64 (s, 2H), 2.56 (d, *J* = 14.4 Hz, 2H), 2.42 (td, *J* = 10.6, 3.5 Hz, 2H), 2.20–2.12 (m, 1H), 1.59–1.52 (m, 1H), 0.86–0.83 (m, 2H), 0.65–0.62 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 208.3, 156.3, 149.1, 57.6, 54.9, 25.9, 25.7, 21.0, 16.3, 4.1 ppm; HRMS (ESI): *m/z* calcd for $C_{16}H_{16}KO_2$ $[M+K]^+$: 279.0782; found: 279.0779. Selected X-ray data: $C_{16}H_{16}O_2$, M = 240.29, Monoclinic, Space group = P21/c, Unit cell: a = a = 7.4362 (3) Å^3, b = 11.7842 (5) Å^3, c = 13.7630 (8) Å^3, α = 90°, β = 102.317 (5) °, γ = 90°, Z = 4, ρcald = 1.355 mg/m^3, F(000) = 512, λ = 0.71073 Å, μ = 0.088 mm^{-1}, Total/unique reflections = 5317/2035, Final *R* indices [*I* > 2sigma (*I*)]: R1 = 0.0440, ωR2 = 0.0960, *R* indices (all data): R1 = 0.0566, ωR2 = 0.1053.

Triquinane 31

Prepared according to the above general procedure using spiro cage dione **30** (100 mg, 0.32 mmol) and diphenyl ether (3 mL) under MWI for 30 min. Column chromatography (10–15% ethyl acetate in petroleum ether) afforded the pure crystalline triquinane **31**. Yellowish brown liquid; Yield: 29 mg (29%); IR (neat, cm^{-1}): 3074, 2952, 2874, 1713, 1637, 1430, 1373, 1354, 1227, 1202, 1176, 1107, 1068, 1044, 995, 915; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.15 (t, *J* = 1.4 Hz, 2H), 5.88–5.78 (m, 2H), 5.10–5.06 (m, 4H), 3.04–3.03 (m, 2H), 2.94–2.89 (m, 6H), 1.66–1.57 (m, 4H), 1.53–1.47 (m, 2H), 1.38–1.32 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 208.2, 156.6, 144.6, 134.3, 117.1, 55.5, 54.7, 52.4, 35.7, 29.6, 23.2 ppm; HRMS (ESI): *m/z* calcd for $C_{21}H_{25}O_2$ $[M+H]^+$: 309.1849; found: 309.1843.

Triquinane 32

Prepared according to the above general procedure using spiro cage dione **30** (100 mg, 0.32 mmol) and diphenyl ether (3 mL) under MWI for 30 min. Column chromatography (20–25% ethyl acetate in petroleum ether) afforded the pure crystalline isomerized triquinane **32**. Yellowish brown liquid; Yield: 47 mg (47%); IR (neat, cm^{-1}): 3077, 2955, 2874, 1713, 1637, 1456, 1429, 1374, 1227, 1202, 1176, 1049, 995, 915; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.13$ (t, $J =$ 1.3 Hz, 1H), 5.86–5.78 (m, 1H), 5.70–5.62 (m, 1H), 5.07–4.95 (m, 4H), 3.66–3.65 (m, 1H), 3.51–3.49 (m, 1H), 2.89 (d, $J = 6.6$ Hz, 2H), 2.76–2.73 (m, 1H), 2.57–2.52 (m, 2H), 2.13–2.03 (m, 2H), 1.84–1.79 (m, 4H), 1.76–1.60 (m, 4H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 205.0$, 203.5, 189.4, 156.2, 143.0, 141.0, 135.5, 134.4, 117.0, 116.8, 57.3, 57.2, 50.6, 50.4, 40.3, 36.0, 32.2, 29.3, 28.7, 25.1, 24.2 ppm; HRMS (ESI): *m/z* calcd for $C_{21}H_{24}NaO_2$ $[M+Na]^+$: 331.1669; found: 331.1669.

General Experimental Procedure for [2+2] Photocycloaddition: Synthesis of Cage Diones Under UV Irradiation (125 W Hg Lamp)

All cage hemiketals **20**, **21** and cage diones **1**, **11**, **25**, **27**, **30**, **35**, and **37** were prepared based on known literature methods using respective Diels-Alder adducts under UV irradiation from 125 W Hg lamp for 30–60 min with pyrex immersion well in dry ethyl acetate solvent.[1–6]

Cage Dione 11[2c]

Colourless crystalline solid; mp: 89–91 °C; (lit. reported[2c] mp 85 °C); ^1H NMR (500 MHz, $CDCl_3$): $\delta = 3.40$ (s, 3H), 3.24–3.20 (m, 1H), 3.08–3.05 (m, 1H), 2.93 (s, 1H), 2.89 (s, 1H), 2.83 (d, $J = 6.4$ Hz, 1H), 2.68–2.58 (m, 2H), 2.00 (d, $J = 11.4$ Hz, 1H), 1.9 (d, $J = 11.4$ Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 210.8$, 209.9, 82.1, 54.7, 53.5, 50.8, 48.5, 43.9, 43.2, 41.9, 36.4 ppm; HRMS (ESI): *m/z* calcd for $C_{12}H_{12}NaO_3$ $[M+K]^+$: 243.418; found: 243.415.

Cage Dione 27[2a,18]

Colourless crystalline solid; mp: 103–105 °C; (lit. reported[2a] mp: 108 °C); ^1H NMR (500 MHz, $CDCl_3$): $\delta = 2.85$ (d, $J = 1.4$ Hz, 2H), 2.77 (s, 2H), 2.72 (s, 2H), 2.02 (d, $J = 11.1$ Hz, 1H), 1.87 (d, $J = 11.1$ Hz, 1H), 1.03 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 214.0$, 54.9, 50.4, 44.4, 43.6, 41.3, 11.6 ppm; HRMS (ESI): *m/z* calcd for $C_{13}H_{14}KO_2$ $[M+K]^+$: 241.0625; found: 241.0623.

Cage Dione 25[24]

Colourless crystalline solid; mp: 76–78 °C; (lit. reported[24] mp: 68–69 °C); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 2.86$ (s, 4H), 2.73 (s, 2H), 2.04 (d, $J = 10.8$ Hz, 1H), 1.97–1.89 (m, 3H), 1.62–1.48 (m, 4H), 1.36–1.30 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 213.7$, 55.1, 49.6, 44.2, 43.6, 41.3, 22.7, 19.3 ppm; HRMS (ESI): *m/z* calcd for $C_{15}H_{17}O_2$ $[M+H]^+$: 229.1223; found: 229.1223.

Cage Hemiketal 20[2a,18]

Colourless crystalline needles; mp: 198–200 °C; (lit. reported[2a] mp: 201–202 °C); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 3.92$ (s, 2H), 3.14 (t, $J =$ 13.0 Hz, 2H), 2.96 (d, $J = 1.5$ Hz, 2H), 2.52 (d, $J = 11.6$ Hz, 1H), 1.82 (d, $J = 11.6$ Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 106.6$, 86.7, 74.6, 52.3, 47.5, 41.7 ppm; HRMS (ESI): *m/z* calcd for $C_{11}H_8Cl_4NaO_3$ $[M+Na]^+$: 350.9120; found: 350.9117.

Cage Hemiketal 21[2a,18]

Light brown crystalline needles; mp: 234–236 °C; (lit. reported[2a] mp: 238–240 °C); ^1H NMR (500 MHz, $CDCl_3$): $\delta = 3.96$ (s, 2H), 3.23 (t, $J = 2.6$ Hz, 2H), 3.07 (d, $J = 1.3$ Hz, 2H), 2.56 (d, $J = 11.8$ Hz, 1H), 1.80 (d, $J = 11.6$ Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 107.0$, 81.7, 68.8, 54.3, 49.7, 41.5 ppm; HRMS (ESI): *m/z* calcd for $C_{11}H_8Br_4KO_3$ $[M+K]^+$: 542.6839; found: 542.6835.

Cage Dione 30[25]

Colourless solid; mp: 73–74 °C; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 5.49$–5.59 (m, 2H), 5.01–5.07 (m, 4H), 2.99 (s, 2H), 2.85 (s, 2H), 2.51 (dd, $J_1 = 14.0$ Hz, $J_2 = 5.6$ Hz, 2H), 2.34–2.32 (m, 2H), 2.21 (dd, $J_1 = 14.0$ Hz, $J_2 = 8.4$ Hz, 2H), 1.66–1.63 (m,4H), 1.53–1.62 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 212.9$, 132.7, 118.6, 65.6, 55.4, 54.0, 51.3, 41.5, 32.4, 30.3, 28.6, 25.7, 25.5 ppm; HRMS (ESI): m/z calcd for $C_{21}H_{24}NaO_2$ $[M+Na]^+$: 331.1669; found: 331.1661.

Cage Dione 35[26]

Colourless crystalline solid; mp: 142–144 °C; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 2.92$ (m, 2H), 2.67 (m, 4H), 2.02–1.97 (m, 2H), 1.92–1.84 (m, 2H), 1.79–1.72 (m, 2H), 1.52 (d, $J = 5.9$ Hz, 1H), 1.50 (d, $J = 6.1$ Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 212.6$, 60.7, 55.2, 44.2, 41.1, 40.7, 27.2, 26.6 ppm; HRMS (ESI) m/z calcd for $C_{14}H_{14}NaO_2$ $[M+Na]^+$ 237.0886; found: 237.0882.

Cage Dione 37[26]

Colourless crystalline solid; mp: 176–178 °C; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 2.90$–2.86 (m, 4H), 2.27–2.26 (m, 2H), 2.05–1.91 (m, 2H), 1.80 (td, $J = 13.0$, 6.9 Hz, 2H), 1.56–1.53 (m, 2H), 0.73–0.63 (m, 4H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 212.5$, 61.3, 55.7, 49.9, 41.5, 37.3, 27.3, 26.8, 5.5, 4.2 ppm; HRMS (ESI) m/z calcd for $C_{16}H_{16}NaO_2$ $[M+Na]^+$ 263.1043; found: 263.1043.

Cage Dione 1[22a]

Colourless crystalline needles; mp: 235–238 °C; (lit. reported[26] mp: 245 °C); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 3.15$ (s, 2H), 2.93–2.91 (m, 2H), 2.80–2.78 (m, 2H), 2.69 (s, 2H), 2.03 (d, $J = 11.5$ Hz, 1H), 1.87 (d, $J = 11.5$ Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 212.2$, 54.8, 44.7, 43.9, 40.6, 38.8 ppm; HRMS (ESI): *m/z* calcd for $C_{11}H_{10}NaO_2$ $[M+Na]^+$: 197.0573; found: 197.0572.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Cage compounds · cycloreversion · triquinanes · photo-thermal metathesis · Diels-Alder reaction · Microwave irradiation

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[27] CCDC 1902281 (**34**) and CCDC 1903722 (**38**) of triquinanes contains supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. For ORTEPs of products **34** and **38**, please see the SI file.

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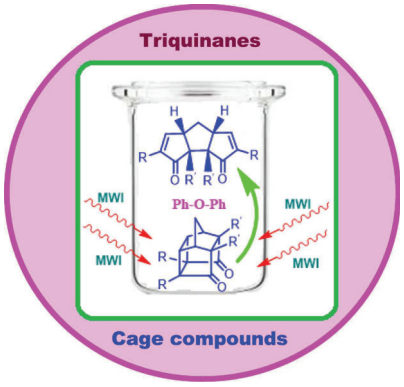
FULL PAPER

Microwave irradiation conditions to assemble a variety of *cis,syn,cis*-triquinane frameworks from cage diones as an alternative to flash vacuum pyrolysis conditions have been reported.



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