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AN EXPEDITIOUS ROUTE TO TRANS FUSED 5-7-6 AND 6-7-6 CARBOCYCLES THROUGH PHOTOISOMERISATION-CYCLOADDITION OF BENZOCYCLOHEPTENONE

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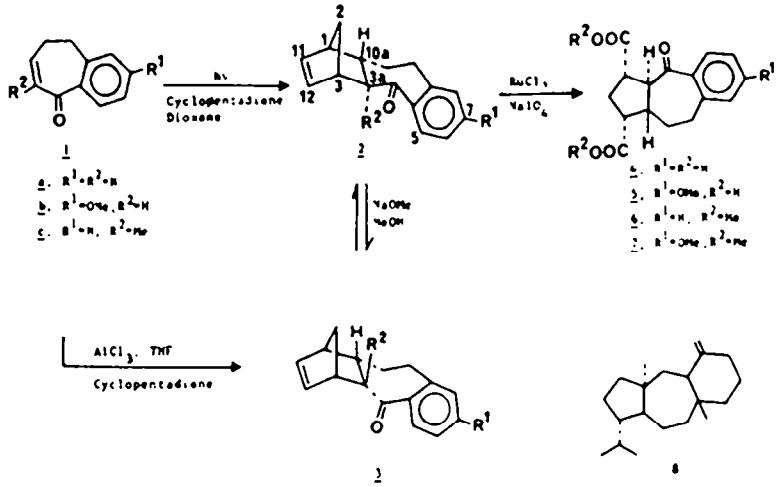
Abstract - Benzocycloheptenones photoisomerise to strained trans-benzocycloheptenones which undergo smooth [4+2] cycloaddition with a variety of dienes. The adducts with cyclopentadiene can be readily transformed to trans fused 5-7-6 ring systems while cycloaddition with isoprene and 2-trimethylsilyloxy-1,3-butadiene produces directly trans fused 6-7-6 ring systems.

The remarkable discovery by Corey[1] and Eaton[2] have demonstrated that 2-cycloheptenone on photoirradiation isomerises to highly strained trans-cycloheptenone which reacts with cyclopentadiene and furan to afford trans adducts. After this observation, 2,6-cycloheptadienone[3] and benzocycloheptenones[4] have been reported to exhibit photoisomerisation. To date, these extraordinarily reactive trans species have never been employed in any synthetic endeavor. Our interest in this area of research arises out of the necessity for a direct synthetic route to the less-accessible trans fused cycloheptanoid compounds especially the 5-7 one, as this structural unit is incorporated in many sesqui-and diterpenes.[5,6] A plethora of elegant strategies for access to the cis 5-7 rings[7] have emerged in the last decade, while only a limited number of multistep strategies for the trans fused 5-7 rings[8] have been reported. The present investigation[9] deals with the scope of photoisomerisation of benzocycloheptenone resulting in the rapid construction of trans fused 5-7-6 and 6-7-6 carbocycles.[10,11]

When a solution of benzocycloheptenone 1a in dioxane was irradiated in the presence of cyclopentadiene, the crystalline trans adduct 2a was formed in excellent yield. The trans geometry of the product was clear from a comparison of its ^{1}H NMR spectrum with that of the cis adduct 3a.[11] The remarkable feature in ^{1}H NMR of 2a is the collapse of the doublet of doublet at δ 3.41 ($J_{3a,10a}$=10.3 and $J_{3a,3}$=3 Hz, attributed to the exo proton at C_{3a} of the cis adduct 3a) to a broad singlet at δ 3.44, thus exhibiting an endo-exo relationship[12] between the protons at C_{3a} and C_{10a} in 2a. The other characteristic spectral feature of the trans adduct is the deshielding of the C_5 proton by 0.7 ppm over the cis adduct 3a, easily explainable from the actual picture of the molecules. Construction of molecular model shows that in 2a, the carbonyl group is held in the same plane with the C_5-proton, an orientation at which the latter experiences the maximum diamagnetic anisotropic effect of the carbonyl group. In 3a, the planes containing the carbonyl group and the C_5-proton bear an angle of approximately 45° forcing the latter away from the deshielding zone. The conclusive evidence that 2a indeed has a trans ring fusion is

obtained from epimerisation study. Treatment of 3a with excess sodium methoxide in refluxing methanol afforded a 1:1 mixture of 3a and its trans epimer which was found identical with the trans adduct 2a. The methoxy analogue 1b, when irradiated

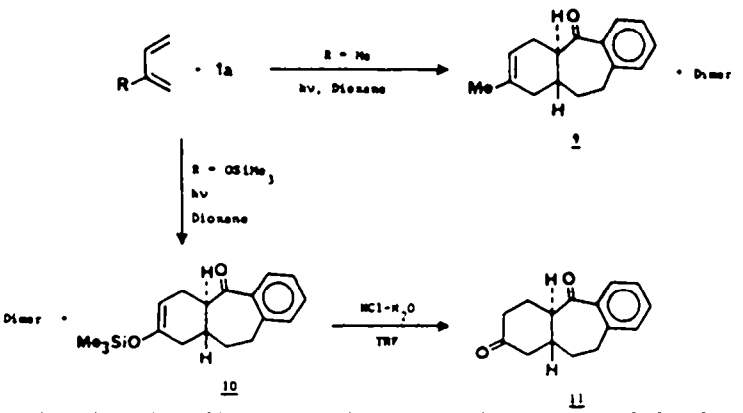


similarly in the presence of cyclopentadiene, gave the crystalline trans adduct 2b in very good yield. For comparative structure analysis the cis adduct 3b was prepared by aluminium chloride catalysed Diels-Alder cycloaddition of 1b with cyclopentadiene. Unambiguous stereochemical assignment to 2b could be made very easily by the appearance of a broad singlet at δ 3.42 in 2b instead of the doublet of doublet at δ 3.38 in 3b as well as by the deshielding of C_5 proton in 2b by 0.6 ppm over the cis adduct 3b.

To determine the effect of alkly substitution on the photoisomerisation of cycloheptenone, 2-methyl analogue 1c was irradiated in an identical fashion in presence of cyclopentadiene. The crystalline trans adduct 2c was obtained only in moderate yield with the formation of minor amount of a crystalline dimeric compound. In analogy to the other trans adducts 2a and 2b, 2c also shows a low field doublet of doublet at δ 8.25 in ^{1}H NMR supporting its trans ring juncture. Thus, alkyl substitution does not inhibit the photoisomerisation of 1. The lower yield of the product reflects the less susceptibility of the substituted dienophile towards cycloaddition as usually observed in thermal cycloaddition reactions.

Transformation of the adducts 2 to the trans fused 5-7 rings were achieved through oxidative fission of the C_{11}, C_{12} double bond. Of the various methods available, only the ruthenium tetraoxide method developed by Sharpless[13] worked cleanly. The adducts 2a,b gave the trans dicarboxylic acids 4 and 5 which were characterised as their dimethyl esters 6 and 7 respectively. The compounds 6 and 7 incorporate the tricarbocyclic unit 8 of the dolastane diterpenes.[10c-f]

To determine the efficacy of the cycloaddition reaction of trans benzocycloheptenone, two other dienes, less reactive than cyclopentadiene, were chosen. For example, irradiation of 1a in presence of isoprene gave the trans adduct 9 in moderate yield with the formation of dimer of 1a. The regiochemical assignment to the only isolable product 9 was made in accord with the results obtained from photochemical[14] as well as thermal[15] cycloaddition of cycloheptenone with isoprene. Similarly, the photoirradiation of 1a in presence of 2-trimethylsilyloxy-1,3-butadiene gave the adduct 10 with simultaneous formation of the dimer of 1a. The adduct 10 was immediately hydrolysed to afford the dione 11. The trans configuration to 9 and 11 was assigned from their mode of formation from 1a.



In summary, the photoirradiation of benzocycloheptenones 1 leads to cis-trans isomerisation of the 2,3-double bond. The resulting trans enones undergo facile cycloaddition with various dienes to lead to trans fused 5-7-6 or 6-7-6 adducts depending on the structure of the diene used during photo-irradiation.

Experimental Section[16]

7-Methoxy benzo[f]cyclohept-2-en-1-one (1b). To a magnetically stirred ice-cold solution of 7-methoxy benzosuberone (500 mg, 2.63 mmol) in anhydrous ether (40 mL), bromine (0.14 mL, 2.7 mmol) was added. Stirring was continued for 2h after which the ether layer was washed successively with saturated aqueous sodium bicarbonate, water and dried (Na_2SO_4). Removal of solvent afforded the 2-bromo derivative (670 mg, 95%); IR (neat) 1675, 1590cm^{-1}; ^{1}H NMR (60 MHz) δ (CCl_4) 1.73-3.06 (m, 6H), 3.80 (s, 3H), 4.70 (dd, H, J = 4 and 6 Hz), 6.66 (s, H), 6.75 (d, H, J = 2 Hz), 7.50 (d, H, J = 8 Hz).

A solution of this crude bromo compound in anhydrous DMF (5 mL) was stirred at 120°C under N_2 for 4 h in presence of LiCl (960 mg, 22 mmol) and Li_2CO_3 (890 mg, 12 mmol). After cooling to room temperature, the reaction mixture was diluted with water (20 mL) and extracted with ether (3 x 30 mL). The ether extract was washed with water (2 x 20 mL) and dried (Na_2SO_4). The residual oil after evaporation of solvent was sublimed to afford 1b (425 mg, 91%); b.p. 146°C (0.3 mm) (bath temp); IR (neat) 1640, 1590 cm^{-1}. ^{1}H NMR δ 2.59 (m, 2H), 3.06 (m, 2H), 3.85 (s, 3H), 6.25 (dt, H, J = 12 and 1.8 Hz), 6.68-6.84 (m, 3H), 7.81 (d, H, J = 8.8 Hz). Anal. calcd. for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found : C, 76.84; H, 6.49.

2-Methyl-benzo[f]cyclohept-2-en-1-one (1c). Following the above procedure of bromination, a solution of 2-methyl benzosuberone (1.5 g, 8.6 mmol) in ether (80 mL) was treated with bromine (0.45 mL, 8.67 mmol) at ice-bath temp for 2.5 h to afford the 2-bromo derivative (2.05 g, 94%); IR (neat) 1680, 1600 cm^{-1}; ^{1}H NMR (60 MHz) δ (CCl_4) 1.01-1.48 (m, 2H), 1.95 (s, 3H), 2.03-2.95 (m, 4H), 6.86-7.42 (m, 4H). Dehydrobromination of the crude bromo derivative in DMF (15 mL) solution was carried out as above by treatment with LiCl (3.08 g, 72.6 mmol) and Li_2CO_3 (2.85 g, 38.5 mmol) at 120°C for 4 h to afford 1c (1.05 g, 78%); b.p. 110°C (0.1 mm) (bath temp); IR (neat) 1630, 1590 cm^{-1}; ^{1}H NMR (60 MHz) δ (CCl_4) 1.96 (s, 3H), 2.30-3.03 (m, 4H), 6.51 (t, H, J = 5 Hz), 6.93-7.63 (m, 4H). This enone (ca. 90% pure) without further characterisation was used in the next step.

Photo-irradiation of benzocycloheptenones (1a-c). 1β,3β,3aα,9,10,10aβ-Hexahydro-1,3-etheno benzo-[f]azulen-4(2H)-one (2a). The general procedure for photo-irradiation and cycloaddition is illustrated by the synthesis of 2a. A solution of benzocycloheptenone 1a[17] (500 mg, 3.16 mmol) in anhydrous dioxane (100 mL) containing freshly distilled cyclopentadiene (5 mL) was irradiated internally through a pyrex immersion well with a Hanovia 450 W medium pressure mercury vapor lamp for 1.5 h under N_2. The reaction mixture was then poured into water and extracted with ether (3 x 50 mL). The ether extract was washed with water (2 x 20 mL) and dried (Na_2SO_4). The residue after removal of solvent was chromatographed through silica gel with petroleum as eluant to afford 2a (540 mg, 77%), m.p. 118°C, R_f 7.49; IR 1670,1600 cm^{-1}; UV_{max} 247 and 288 nm (log ε 4.17 and 3.45); ^{1}H NMR δ 1.38

(br d, 2H, J = 8 Hz), 1.62 (dd, H, J = 8 and 2 Hz), 2.01 (m, 2H), 2.22 (br d, H, J = 8 Hz), 2.83 (br s, H), 2.98 (m, 2H), 3.44 (br s, H), 6.19 (dd, H, J = 5 and 3 Hz), 6.44 (dd, H, J = 5 and 3 Hz), 7.28-7.54 (m. 2H), 8.17 (dd, H, J = 8 and 2 Hz). Anal. calcd. for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found : C, 85.95; H, 7.32.

1β,3β,3aα,9,10,10aβ-Hexahydro-1,3-etheno-7-methoxy benzo[f]azulen-4(2H)-one (2b). Irradiation of a solution of 1b (420 mg, 2.23 mmol) in dioxane (100 mL) containing cyclopentadiene (4 mL) for 3.5 h afforded 2b (370 mg, 65%), m.p. 86°C; IR 1665, 1595 cm^{-1}; UV_{max} 224 and 275 nm (log ε 4.09 and 4.12); ^1H NMR δ 1.32 (m, 2H), 1.61 (m, H), 2.00 (m, 2H), 2.18 (br d, H, J = 8 Hz), 2.82 (br s, H), 2.96 (m, 2H), 3.42 (br s, H), 3.86 (s, 3H), 6.16 (dd, H, J = 5 and 3 Hz), 6.42 (dd, H, J = 5 and 3 Hz), 6.78 (d, H, J = 2 Hz), 6.89 (dd, J = 8 and 2 Hz), 8.16 (d, H, J = 8 Hz). Anal. calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found : C, 80.46; H, 7.21.

1β,2,3β,9,10,10aβ-Hexahydro-3α-methyl-1,3-etheno benzo[f]azulen-4-one (2c). Irradiation of a solution of 1c (440 mg, 2.55 mmol) in dioxane (100 mL) containing cyclopentadiene (5 mL) for 2.5 h afforded 2c (155 mg, 25%), m.p. 95°C; IR 1670, 1595 cm^{-1}; UV_{max} 248 and 288 nm (log ε 4.15 and 3.14); ^1H NMR δ 1.11 (s, 3H), 1.28-1.58 (m, 3H), 1.98 (m, H), 2.34 (m, H), 2.69 (br s, H) 3.01 (q, H, J = 8 Hz), 3.22 (q, H, J = 8 Hz), 3.40 (br s, H), 6.33 (m, 2H), 7.24-7.52 (m, 3H), 8.25 (dd, H, J = 8 and 2 Hz). Anal. calcd. for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found : C, 85.52; H, 7.41.

During chromatography of the reaction mixture a second component (37 mg) was obtained, m.p. 210-214°C; ^1H NMR δ 1.08 (d, 3H, J = 8 Hz), 1.32-1.64 (m, 2H), 1.92-2.14 (m, 3H), 2.29 (dd, H, J = 10.4 and 16.8 Hz), 2.62-2.94 (m, 5H), 5.27 (d, H, J = 2 Hz), 6.14 (d, H, J = 2 Hz), 7.08-7.52 (m, 7H), 7.82 (dd, J = 8 and 2 Hz). Anal. calcd. for $C_{24}H_{24}O_2$: C, 83.69; H, 7.02. Found : C, 83.55; H, 7.27.

Irradiation of 1a in presence of isoprene. Synthesis of (9). A solution of 1a (100 mg, 0.63 mmol) in dioxane (11 mL) containing isoprene (1.3 mL, 12.6 mmol) was irradiated externally in a pyrex vessel for 2 h. Removal of volatile materials followed by chromatography through silica gel with 5% ethyl acetate-hexane afforded 9 (50 mg, 35%); ^1H NMR δ 1.62 (s, 3H), 1.77-2.08 (m, 6H), 2.57-3.12 (m, 4H), 5.32-5.38 (m, H), 7.15-7.33 (m, 3H), 7.68 (d, H, J = 7.8 Hz), mass spectrum m/z (relative intensity) 226.1359 (M^+, 33, calcd. for $C_{16}H_{18}O$, 226.1358), 211 (25), 197 (72), 193 (39), 183 (34), 179 (25), 155 (21), 141 (51), 133 (24), 131 (27), 129 (76), 128 (49), 117 (100), 91 (93), 88 (51), 77 (57) and benzocycloheptenone dimer[18] (32 mg, 15%), m.p. 130-142°C; ^1H NMR δ 1.89-2.12 (m, 2H), 2.18-2.45 (m, 4H), 2.63-3.32 (m, 6H), 7.18-7.60 (m, 7H), 7.94 (dd, H, J = 8 and 2 Hz). Anal. calcd. for $C_{22}H_{20}O_2$: C, 83.51; H, 6.37. Found : C, 83.52; H, 6.52.

Irradiation of 1a in presence of 2-trimethyl silyloxy-1,3-butadiene. Synthesis of (11). A solution of 1a (100 mg, 0.63 mmol) in dioxane (11 mL) containing 2-trimethyl silyloxy-1,3-butadiene (0.8 g, 5.6 mmol) was irradiated externally in a pyrex vessel for 5 h under N_2. Removal of dioxane followed by silica gel chromatography with 3% ethyl acetate-hexane afforded three fractions : 1st fraction is a liquid (110 mg) which contains the adduct 10; 2nd fraction (20 mg) is the starting enone 1a and the 3rd fraction is a dimer (20 mg). The first fraction (110 mg) in THF (2 mL) was treated with H_2O (0.5 mL) and HCl (12 N, 0.5 mL) at r.t. for 5 h. The organic material in it was extracted with ether. The ether extract was washed with saturated aqueous sodium bicarbonate, brine and dried (Na_2SO_4). Evaporation of ether followed by chromatography (25% ethyl acetate-hexane) afforded 11 (42 mg, 37% based on consumed 1a), m.p. 91°C; IR 1710, 1670, 1590 cm^{-1}. ^1H NMR δ 1.82-2.57 (m, 9H), 2.88-3.28 (m, 3H), 7.25-7.46 (m, 3H), 7.75 (dd, H, J = 7.4 and 1.5 Hz); mass spectrum m/z (relative intensity) 228.1141 (M^+, 83.8, calcd for $C_{15}H_{16}O_2$, 228.1151), 199(29), 172 (22), 159 (45), 146 (37), 132 (32), 131 (91), 130 (29), 129 (41), 128 (37), 118 (76), 116 (27), 104 (64), 103 (37), 91 (100), 90 (80), 89 (30), 77 (42).

Epimerisation of 3a. The cis ketone 3a (70 mg, 0.31 mmol) was refluxed with 2% NaOMe in MeOH (2 mL, 0.74 mmol) under N_2 for 2 h. The reaction mixture on dilution with water was extracted with ether. The ether extract after drying (Na_2SO_4) was concentrated to afford a solid (58 mg, 82%) which was found to be a mixture of 2a (R_t 16.96) and 3a (R_t 18.11) in a ratio of 55:45 as determined by GC [10% UCW-982 on 80-100 WAW-DMCS (20" x ⅛") at 150°C].

Catalysed Diels-Alder reaction of 1b. 1β,3β,3aβ,9,10,10aβ-Hexahydro-1,3-etheno-7-methoxy benzo-/f/azulen-4(2H)-one (3b). Cyclopentadiene (7 mL) was directly distilled into a solution of 1b (850 mg, 3.35 mmol) in THF (7 mL) containing aluminium chloride (340 mg, 2.5 mmol) at 0°C. The light brown solution was stirred at that temperature for 1.5 h. After diluting with water, the reaction mixture was extracted with ether (3 x 50 mL). The ether extract was washed with water (2 x 20 mL) and dried (Na_2SO_4). Removal of solvents followed by column chromatography (5% ethyl-acetate-petroleum) afforded 3b (850 mg, 54%), m.p. 80°C; ^{1}H NMR δ 1.11-1.65 (m, 3H), 2.0 (br d, H), 2.42-2.71 (m, H), 2.82 (br s, H), 3.07-3.31 (m, 3H), 3.38 (dd, H, J = 10.5 and 3 Hz), 3.80 (s, 3H), 6.02 (dd, H, J = 5.6 and 2 Hz), 6.51 (dd, H, J = 5.6 and 1.8 Hz), 6.64-6.78 (m, 2H), 7.52 (d, H, J = 8.7 Hz). Anal. calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found : C, 80.39: H, 7.66.

1β,3β,3aα,9,10,10aβ-Hexahydro-4(2H)-oxo benzo/f/azulene-1,3-dicarboxylic acid (4) and its dimethyl ester (6). A mixture of carbon tetrachloride (3 mL), acetonitrile (3 mL), water (4.2 mL), sodium metaperiodate (480 mg, 2.24 mmol), olefin 2a (100 mg, 0.44 mmol), and ruthenium trichloride hydrate (5 mg) was stirred vigourously at room temperature for 4 h. The residue after rotary evaporation of the solvents from the reaction mixture was extracted with ethyl acetate (4 x 25 mL). The organic extract was washed with 2% aqueous KOH. The basic aqueous washing was acidified with 6N HCl and then extracted with ethyl acetate (4 x 20 mL). The organic extract was washed with brine and dried (Na_2SO_4). Removal of solvent followed by crystallization of the residue from ethyl acetate afforded the dicarboxylic acid 4 (75 mg, 71%), m.p. 185°C (dec.); IR 1705, 1660, 1595 cm^{-1}. Anal. calcd. for $C_{16}H_{16}O_5$: C, 66.66; H, 5.59. Found : C, 66.89; H, 5.26.

The acid 4 (55 mg) was treated with an excess of ether solution of diazomethane for 5 min. After removal of ether, the crude product was filtered through neutral alumina (50% ether-petroleum) to afford the methyl ester 6 (58 mg, 95%), m.p. 96°C; IR 1735, 1720, 1670, 1595cm^{-1}; ^{1}H NMR δ 1.66-2.44 (m, 6H), 2.73-2.94 (m, H), 3.0-3.16 (m, 2H), 3.40 (q, H, J = 8 Hz), 3.68 (s, 3H), 3.76 (s, 3H), 7.21-7.49 (m, 3H), 7.78 (dd, H, J = 8 and 2 Hz). Anal. calcd. for $C_{18}H_{20}O_5$: C, 68.34; H, 6.37. Found : C, 68.55; H, 6.38.

1β,3β,3aα,9,10,10aβ-Hexahydro-4(2H)-oxo-7-methoxy benzo/f/azulene-1,3-dicarboxylic acid (5) and its dimethyl ester (7). A mixture of carbon tetrachloride (3 mL), acetonitrile (3 mL), water(4.2 mL), sodium metaperiodate (425 mg, 1.98 mmol), olefin 2b (100 mg, 0.39 mmol) and ruthenium trichloride hydrate was stirred vigorously for 4 h. Work up of the reaction mixture as for the preparation of 4, afforded the dicarboxylic acid (76 mg, 74%), m.p. 186°C (dec.); IR 1730, 1715, 1655, 1595 cm^{-1}. Anal. calcd. for $C_{17}H_{18}O_6$: C, 64.14; H, 5.70. Found : C, 63.89; H, 5.40.

The acid 5 (50 mg) was esterified with diazomethane as above to afford the dimethyl ester 7 (50 mg, 91%), m.p. 78°C; IR 1735, 1725, 1670, 1595 cm^{-1}; ^{1}H NMR δ 1.76-2.44 (m, 6H), 2.80-2.88 (m, H), 2.99-3.25 (m, 2H), 3.35 (q, H, J = 8 Hz), 3.70 (s, 3H), 3.76 (s, 3H), 3.86 (s, 3H), 6.72 (d, H, J = 2 Hz), 6.86 (dd, H, J = 8 and 2 Hz), 7.70 (d, H, J = 8 Hz). Anal. calcd. for $C_{19}H_{22}O_6$: C, 65.88; H, 6.40. Found : C, 65.86; H, 6.27.

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16. Melting points were recorded in sulfuric acid bath and are uncorrected. IR spectra were recorded in KBr pellet on a Perkin-Elmer 298 spectrophotometer. Unless otherwise stated, ^{1}H NMR spectra were recorded at 200 MHz against Me_4Si as an internal standard in $CDCl_3$ solution on a Varian XL-200 spectrometer. High resolution mass spectra were obtained by courtsey of Prof. R.G. Salomon of Chemistry Department at Case Western Reserve University and were recorded on a DS-50S Mass spectrometry data system. Gas chromatography was carried out on a Shimadzu GC-9A model using OV-17 on 1.5% shimalite W 80-100 silanized column (6 m x 3 mm) unless otherwise stated. UV spectra were recorded on a Beckman DU spectrometer in ethanol solution. Column chromatography was performed through silica gel (60-200 mesh). Petroleum refers to fraction of petroleum ether boiling in the range 60-80°C.

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18. The structure elucidation of the dimers obtained by photoirradiation of 1a has been reported by Hart et al (Reference 4b).