Photoisomerization of Triquinacene Congeners

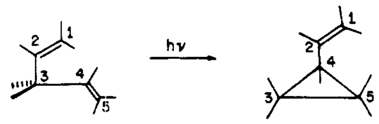
Leo A. Paquette,* James D. Kramer,[1a] Paul B. Lavrik,[1b] and Matthew J. Wyvratt[1c]

Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210

Received July 28, 1976

The triplet-sensitized photochemical rearrangements of 2,3-dihydrotriquinacene (**2**), nortriquinacene (**7**), and benzotriquinacene (**13**) are described. These molecules, which comprise rigid structures having fixed parallel double bonds, undergo formal [$_\pi2 + _\pi2$] cycloaddition by a process believed to be stepwise. The initial bonding scheme is identical with that which is utilized in the di-π-methane rearrangement, but ultimate vinylcyclopropane formation is not realized, probably because of structural reasons. The synthesis of **13** was achieved by a convenient benzoannulation sequence starting with 2,3-dihydrotriquinacen-2-one (**9**).

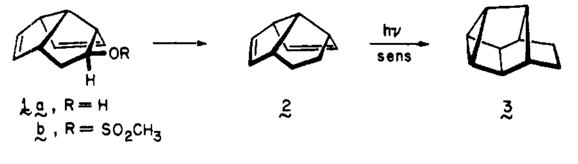
The last decade has witnessed extensive exploration of the so-called di-π-methane rearrangement,[2] that process by which the excited state of a 1,4-diene transmutes by 1,2-vinyl migration and ring closure to a vinylcyclopropane. These studies have played an important role in the development of our understanding of structural and substituent effects on excited-state multiplicity, control of regiospecificity, and preferred rearrangement stereochemistry. Of particular interest to us have been those photoisomerizations where the customary course of the di-π-methane rearrangement is rerouted at some intermediate stage for one of several reasons. As an example, it is entirely plausible that many rigid dienes may be of such geometry that the requisite molecular distortion or steric strain required to arrive at their vinylcyclopropane photoisomers would prove inimical to this process and cause conversion instead to a structurally rather different product. Suggestive evidence has been provided particularly by Hart,[3] and less directly by Gorman,[4] Kaupp,[5] Freeman,[6] and Linstrumelle[7] that bicyclo[3.3.0]octa-2,7-diene and bicyclo[3.2.0]hepta-2,6-diene ring systems incorporate folded molecular geometries with atomic distances and orbital dihedral angles highly unfavorable to direct [$_\pi2 + _\pi2$] cycloaddition. Nevertheless, the prevailing proximity effects are now such that operation of the normal di-π-methane rearrangement could be diverted without formation of a discrete vinylcyclopropane intermediate.



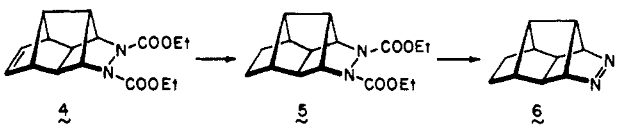
For these reasons, an examination of the photochemistry of several highly cup-shaped molecules of the triquinacene family was undertaken. An ancillary goal was to gain access to strained molecules of rather unusual structure for utilization in other research programs.

Results

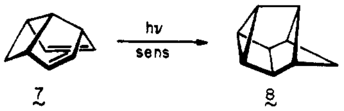
2,3-Dihydrotriquinacene (**2**), the first example studied, was prepared in 85% yield by conversion of alcohol **1a**[8] to its mesylate followed by reduction of **1b** with lithium aluminum hydride. Irradiation of **2** in benzene solution containing 5% acetone as sensitizer with Corex filtered light (Hanovia 450-W) for 85 h afforded a single volatile photoproduct in 40% yield. Even at such long reaction times, 10% of **2** remained unchanged. Separation of the two components was achieved by elution of the concentrated photolysate through silver nitrate (5%) impregnated silica gel with pentane. The mass spectrum and elemental composition of the pure photoproduct indicated it to be isomeric with **2**. The absence of trigonal carbons was apparent from the lack of olefinic protons in its ^{1}H NMR spectrum. On this basis and the appearance in its ^{13}C spectrum of only six lines, **3** was assigned the symmetrical structure indicated.



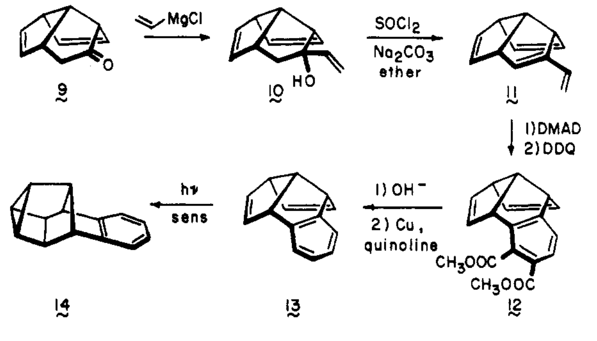
An unequivocal synthesis of **3** was accomplished by catalytic hydrogenation of **4**,[9] hydrolysis–oxidation of the resulting dihydro derivative (**5**) to give azo compound **6**, and nitrogen extrusion from **6** by irradiation through Pyrex at 3500 Å in pentane solution. Under these conditions, there was produced 37–40% of **2**, 50–55% of **3**, and two minor unidentified products. As in the case of a structurally related azo compound,[9] formation of the principal photoproducts can be rationalized in terms of an intermediate 1,3 biradical which either closes to form a bicyclo[2.1.0]pentane moiety or experiences central bond cleavage to generate a pair of olefinic bonds.



The fate of nortriquinacene (**7**)[10] proved to be entirely comparable. Its irradiation under the predescribed conditions for 65 h caused almost complete conversion to a single volatile product (14%) with simultaneous polymer formation. Structural assignment to **8** follows from the combined spectral evidence. While its proton magnetic resonance spectrum is characterized by six groups of upfield signals (see Experimental Section) bearing many close similarities to those which characterize **3**, its ^{13}C spectrum features uniquely those six peaks required by the molecular symmetry.[11]



At this point, attention was turned to benzotriquinacene (**13**). To elaborate this structure, use was made of the ketone benzoannulation scheme developed earlier in this laboratory.[14] The action of vinylmagnesium chloride converted ketone **9**[8,15]



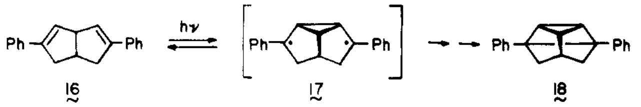
into vinyl alcohol **10** whose dehydration afforded vinyltriquinacene (**11**). Addition of dimethyl acetylenedicarboxylate to **11** followed by dehydrogenation with DDQ led to adduct **12** which underwent ready saponification and copper-catalyzed decarboxylation to give **13**. The triquinacene nature of this hydrocarbon is readily apparent from the rather simple ^{1}H NMR spectrum ($CDCl_3$) which consists of two singlets at δ 7.12 (4 H, aromatic) and 5.67 (4 H, vinylic) in addition to a four-proton multiplet (4.47–3.73) arising from the bridgehead protons. With the exception of the anisotropic effects introduced by the benzene ring, close agreement exists with the values reported in the literature for the parent ring system.[16]

Despite the fact that **13** is intrinsically capable of excited state benzo–vinyl as well as vinyl–vinyl bonding, no evidence was found for the first pathway under the sensitized conditions required for photoisomerization. This behavior is in line with the structure–multiplicity relationships generally adhered to in di-π-methane rearrangements.[2] When the progress of reaction was monitored by VPC, disappearance of the majority (96%) of **13** and formation of **14** as the only volatile product in low (8.5%) yield was observed after 90 h of irradiation. Separation of **14** from polymer was achieved by sequential column and gas chromatography. The ^{1}H NMR spectrum ($CDCl_3$) of this stable, oily hydrocarbon shows the expected downfield aromatic singlet (δ 7.01, 4 H) in addition to multiplets at 3.32 (3 H), 2.32–2.26 (4 H), and 1.70–1.47 (1 H) attributable to (a) the benzylic and apical protons, (b) cyclobutyl hydrogens, and (c) remaining cyclopropyl proton, respectively. In its upfield region, this spectrum is highly reminiscent of that exhibited by **15**.[9] The paired ^{13}C signals of **14** likewise accord with the C_s symmetry of the molecule.

15

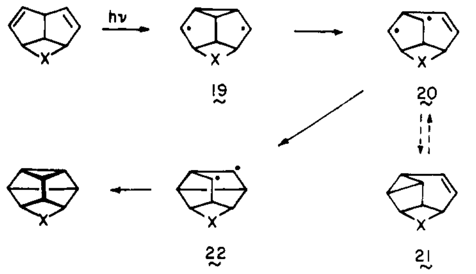
Discussion

The photoisomerizations of **2**, **7**, and **13** proceed exceptionally slowly in the absence of sensitization with production of polymers. The efficiency of their sensitized reactions suggests that triplet excited states intervene. Direct $[_{\pi}2 + _{\pi}2]$ ring closures seem highly unlikely in these examples because of the large distance separating the central sp^2-hybridized carbons and the poor dihedral angle relationships of their pπ orbitals. Rather, the initial step is preferably viewed as proceeding by bonding of the proximal olefinic centers in a fashion analogous to that which triggers di-π-methane rearrangements, since a minimum of geometric change is involved (Scheme I). If such biradicals do intervene, there would be obvious reason to expect enhancement of reaction efficiency upon phenyl substitution as in **16**. In this regard, Kaup and Krieger have found convincing evidence for generation of **17** as the short-lived electronic intermediate which ultimately leads to **18**.[5] Primarily due to the residual large separation of the radical centers in **17** and **19**, there exists a greater likelihood for cleavage of the three-membered ring to give **20** than of formation of a tetracyclic framework.



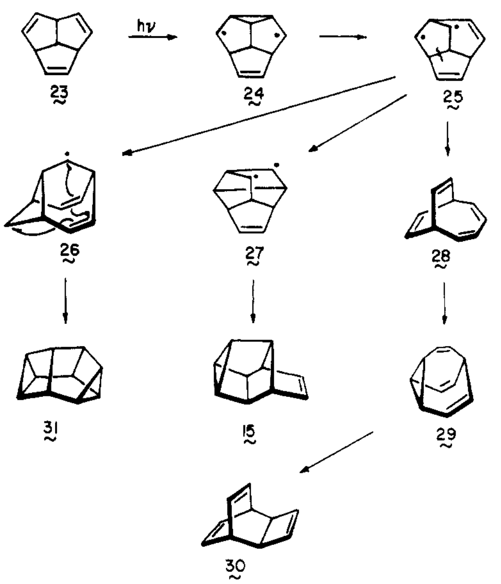
Subsequent collapse of the biradical centers in **20** would deliver the normal di-π-methane products **21**. However, no evidence was obtained for generation of compounds of this type. If such molecules had been formed as discrete intermediates in those examples where X = CH_2 or $-CH_2CH_2-$, no precedent exists for their photolability under the reaction conditions. This route to the observed products, clearly a two-photon pathway, is both difficult to dismiss and to substantiate without access to the hydrocarbons **21**.

Scheme I



At this point, it is appropriate to discuss the photochemistry of triquinacene (**23**). Under the conditions employed in this study, **23** underwent polymerization exclusively. At the appearance of Bosse and de Meijere's paper,[17] further work was discontinued in our laboratory. The Göttingen group observed that direct irradiation of **23** for 30–50 h in pentane solution at −40 °C in a falling film apparatus gave a mixture of eight products with **15** and **28–31** predominating (Scheme II). We suggest that a comparable pair of biradicals (**24** and **25**) intervene. Because of the additional available double bond in **25**, redirection of the customary electronic reorganization occurs as the direct result of internal σ bond cleavage. Once access is gained to **28** (9%), its photoequilibration with bullvalene (**29**, 5%) and tricyclodecatriene **30** (6%) can be fully anticipated.[18] Perhaps as the direct result of singlet state reactivity, **25** is further capable of 1,2-alkyl shift to generate **26**, the likely precursor to **31** (49% relative yield).

Scheme II



The formation of **15** (26%) is the only common link to the present work. If these reactions are stepwise as depicted, the altered geometry of **20** (Scheme I) and **25** (Scheme II) brings the radical centers and the π bond into proximity adequate for conjoining of the two central carbons. The structural features of **22** and **27** are conducive to formation of the final bicyclopentane bond.

The weight of evidence which is presently available suggests, but does not of course prove, that a multistep mechanism occurs in those intramolecular $[_{\pi}2 + _{\pi}2]$ cycloadditions involving rigid molecules having fixed parallel double bonds. Our experience with such reactions is that they lack generality, particularly when polar substituents are present elsewhere in the molecule. For example, alcohol **1a**, ether **32**,

32

33

and epoxide **33** gave no volatile products, but only polymerized when subjected to sensitized irradiation.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 467 spectrophotometer. The ^{1}H NMR spectra were determined with Varian A-60A and HA-100, as well as Bruker HX-90, instruments, and apparent splittings are given in all cases. The ^{13}C spectra were also run on the Bruker spectrometer. Mass spectra were measured on an AEI-MS9 spectrometer at an ionizing energy of 70 eV. Preparative scale VPC separations were performed on a Varian Aerograph Model A-90-P3 instrument equipped with thermal conductivity detectors. Microanalytical determinations were performed at the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

2,3-Dihydrotriquinacene (2). To an ice-cold solution of **1a**[8] (2.00 g, 13.5 mmol) in purified dichloromethane (20 ml) was added 2.4 ml (17.6 mmol) of triethylamine. Methanesulfonyl chloride (1.7 g, 14.9 mmol) dissolved in 4 ml of dichloromethane was introduced dropwise at 0 °C. After 20 min at this temperature, water (20 ml) was added and the organic layer was washed with 10% hydrochloric acid (2 × 25 ml), saturated sodium bicarbonate solution (2 × 25 ml), and brine prior to drying and evaporation. The crude mesylate (2.85 g, 93%) was dissolved in anhydrous ether (50 ml) and this solution was added dropwise to a slurry of lithium aluminum hydride (700 mg, 18.4 mmol) in ether (50 ml). The slightly exothermic reaction was completed by stirring overnight at 25 °C followed by 6 h at the reflux temperature. The excess hydride was quenched by sequential addition of water (0.7 ml), 15% sodium hydroxide solution (0.7 ml), and water (2.1 ml). The precipitated white solid was removed by filtration and washed well. The combined filtrates were dried and carefully evaporated. The concentrate was dissolved in pentane, filtered through a 1.5 × 0.75 in. plug of neutral alumina, and the solvent was removed by careful distillation through an 8-in. Vigreux column. There remained 1.5 g (85%) of **2** whose ^{1}H NMR spectrum was identical with that reported earlier.[19]

Photoisomerization of 2. A solution of **2** (600 mg) in 5% acetone-benzene (600 ml) was deoxygenated with nitrogen for 30 min. Irradiation for 85 h with a 450-W medium-pressure Hanovia lamp through Corex optics yielded a yellow solution containing suspended solid. VPC analysis (10 ft × 0.125 in. 15% Carbowax 20M on Chromosorb P, 100 °C) revealed that 10% of **2** remained and that a single photoproduct had been formed in 40% yield. The photolysate was filtered and the clear yellow solution was carefully concentrated to a volume of 20 ml by distillation through a 45-cm Vigreux column. Pentane (10 ml) was added and the solution passed through a column of 5% silver nitrate on silica gel (40 g) with pentane elution. The colorless eluate, which contained no **2** (VPC analysis), was concentrated to a volume of 2 ml by spinning band distillation. Preparative VPC purification (4 ft × 0.25 in. 10% SF-96 on Chromosorb P, 80 °C) afforded 140 mg (23%) of **3** as a colorless, volatile liquid: $\delta_{\mathrm{Me_4Si}}$ (CDCl$_3$) (100 MHz) 2.45–2.27 (m, 1), 2.27–2.14 (m, 2), 2.15 (s, 2), 2.03–1.96 (m, 2), 1.74–1.54 (m, 1), 1.54–1.26 (m, 2), and 1.02–0.26 (m, 2); ^{13}C NMR (CDCl$_3$) 53.79, 47.80, 42.73, 28.38, 25.14, and 22.44 ppm.

Anal. Calcd for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 90.64; H, 9.26.

Diethyl Octahydro-3,4,7-metheno-1*H*-pentaleno[2,1-*c*]-pyrazole-1,2(3*H*)-dicarboxylate (5). A solution of **4** (1.05 g, 3.47 mmol)[9] in 10 ml of absolute ethanol containing 32 mg of 5% palladium on carbon catalyst was hydrogenated at an initial pressure of 50 psi of hydrogen. After 2 h, the mixture was filtered through a Celite pad and the filtrate was concentrated to yield a clear oil which solidified (1.04 g, 98%). Recrystallization from ether/pentane afforded **5** as white crystals: mp 66.5–68 °C; $\nu_{\max}$ (CCl$_4$) 1744, 1702, and 1315 cm^{-1}; $\delta_{\mathrm{Me_4Si}}$ (CDCl$_3$) 4.38 (br s, 2), 4.18 (q, J = 7 Hz, 4), 2.31 (m, 3), 2.08 (m, 3), 1.57 (br s, 4), and 1.28 (t, J = 7 Hz, 6).

Anal. Calcd for $C_{16}H_{22}N_2O_4$: C, 62.72; H, 7.24; N, 9.14. Found: C, 62.46; H, 7.25; N, 9.19.

3a,3b,4,5,6,6a,7,7a-Octahydro-3,4,7-metheno-3*H*-pentaleno-[2,1-*c*]pyrazole (6). A solution of **5** (0.631 g, 2.062 mmol) and potassium hydroxide (1.349 g, 20.8 mmol) in 80 ml of 2-propanol was heated at reflux under nitrogen for 2 h. The heterogeneous mixture was acidified at 0 °C to a pH of 2 with 3 N hydrochloric acid. After warming to room temperature, the acidic mixture was neutralized with aqueous 3 N ammonium hydroxide solution, and to this heterogeneous mixture was added 1.90 g (0.0206 mol) of manganese dioxide. After being stirred at room temperature for 2.5 h, the mixture was diluted with 100 ml of dichloromethane and filtered, and the filtrate was treated with 500 ml of water. After separation of the layers, the aqueous phase was extracted with dichloromethane (5 × 75 ml) and the combined organic layers were washed with water (3 × 125 ml) and brine before drying. The solvent was removed at atmospheric pressure to yield a reddish oil (387 mg) which was either recrystallized from pentane or chromatographed on silica gel (30% ether/petroleum ether) prior to sublimation at 80 °C (35 mm). There was obtained 250 mg (76%) of **6** as white plates: mp 44.5–45.5 °C; $\nu_{\max}$ (CCl$_4$) 2865, 1500, and 1252 cm^{-1}; $\delta_{\mathrm{Me_4Si}}$ (CDCl$_3$) 5.08 (d, J = 3 Hz, 2), 2.60 (br s, 2), 2.47 (m, 1), 2.02 (m, 1), and 1.56 (br s, 6); *m/e* calcd 160.1000, obsd 160.1003.

Anal. Calcd for $C_{10}H_{12}N_2$: C, 74.96; H, 7.55. Found: C, 74.57; H, 7.51.

Photolysis of 6. A stirred, degassed solution of **6** (304 mg, 1.90 mmol) in 125 ml of purified pentane contained in a Pyrex tube was irradiated under nitrogen in a Rayonet reactor equipped with 3500 Å lamps for 23 h. The pentane solution was concentrated through a vacuum-jacketed Vigreux column at atmospheric pressure. VPC analysis of the concentrate (10 ft × 0.125 in. Carbowax 20M on Chromosorb P, 80 °C) showed 37–40% of dihydrotriquinacene (**2**), 50–55% of **3**, together with 3–4% and 7–8% of two minor, unidentified products which had been formed.

The crude mixture was chromatographed on a silica gel column (16 × 2.5 cm). Pentane elution achieved partial separation of **2** from **3**. Preparative VPC (10 ft × 0.25 in. 10% Carbowax 20M on Chromosorb G, 110 °C) afforded the pure hydrocarbons, the spectra of which were superimposable on those of the original samples.

Photoisomerization of Tricyclo[4.2.1.0^{3,9}]nona-4,7-diene (Nortriquinacene, 7). A solution of 236 mg (2.0 mmol) of **7**[10] dissolved in 200 ml of 5% acetone in benzene was flushed free of oxygen by bubbling nitrogen through the solution for 30 min. The stirred solution was irradiated through a Corex filter with a 450-W Hanovia medium-pressure lamp. The progress of the reaction was monitored by VPC (10 ft × 0.125 in. 15% Carbowax 20M on Chromosorb P, 90 °C). After 65 h, 5% unreacted starting material remained and 14% of a single volatile photoproduct had been formed. The solvent was removed by careful distillation through a 24-in. Vigreux column until 3 ml of solution remained. The concentrate was chromatographed through a small Florisil column using pentane as the eluent. The resulting colorless solution was again concentrated to a 3-ml volume by fractional distillation at room atmosphere and photoproduct **8** was isolated by preparative VPC (6 ft × 0.25 in. 10% OV-11 on Chromosorb W, 95 °C): $\nu_{\max}$ (neat) 3050, 2980, 2880, 1280, 1265, 1235, 1210, 1190, 1145, 935, 795, 765, and 725 cm^{-1}; $\delta_{\mathrm{Me_4Si}}$ (CDCl$_3$) 2.74 (br s, 3), 2.45 (br s, 2), 2.22 (br d, 2), 1.75 (m, 1), 1.45 (m, 1), 0.85 (d, J = 8.0 Hz, 1); ^{13}C NMR (CDCl$_3$) 54.1, 53.2, 41.8, 31.0, 29.8, 28.1 ppm; *m/e* calcd 117.0704, obsd 117.0707.

Anal. Calcd for C_9H_{10}: C, 91.47; H, 8.53. Found: C, 91.61; H, 8.60.

2-Vinyl-2,3-dihydrotriquinacen-2-ol (10). A solution of 1.0 g (6.8 mmol) of 2,3-dihydrotriquinacen-2-one (**9**)[8,15] in 10 ml of dry tetrahydrofuran was added dropwise to a solution of vinylmagnesium chloride freshly prepared from 333 mg (13.7 mg-atoms) of finely cut magnesium and excess vinyl chloride in 20 ml of dry tetrahydrofuran.[20] The reaction mixture was heated briefly to the reflux temperature and stirred at room temperature for 3 h. Excess Grignard reagent was destroyed by careful addition of water and the resulting solution was evaporated. The residues were partitioned between ether (50 ml) and water (50 ml) and the emulsion was broken by dropwise addition of 10% hydrochloric acid. The aqueous layer was separated and extracted with additional ether (2 × 50 ml). The combined ether solutions were washed with saturated sodium bicarbonate solution, dried, and evaporated to give 1.5 g of yellow oil. Its chromatographic purification on 20 g of silica gel (elution with 25% ether in pentane) afforded 1.0 g (85%) of pure **10**. VPC analysis (10 ft × 0.125 in. 10% SF-96 on Chromosorb P, 125 °C) indicated the alcohol to be essentially pure endo isomer (>98%): $\nu_{\max}$ (neat) 3400, 3050, 2955, 2890, 1640, 990, 920, 848, 733, and 715 cm^{-1}; $\delta_{\mathrm{Me_4Si}}$ (CDCl$_3$) 6.4–4.9 (m, 7, characteristic terminal vinyl pattern superimposed on 4 H multiplet), 4.0–3.8 (br m, 1), 3.8–2.9 (m, 3), 2.3–1.6 (m, 3, the OH proton superimposed upon a symmetrical five-line multiplet).

Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.38; H, 8.31.

2-Vinyltriquinacene (11). To a solution of **10** (100 mg, 0.57 mmol) in 5 ml of anhydrous ether was added 1.0 g of solid sodium carbonate and 150 μl (250 mg, 2.1 mmol) of thionyl chloride. The mixture was stirred under a nitrogen atmosphere for 36 h at room temperature and filtred. The filtrate was washed with water and saturated sodium bicarbonate solution, dried, and evaporated to yield 80 mg of yellow oil. Chromatography on 1.0 g of silica gel with pentane elution afforded 60 mg (90%) of **11**. Alternatively, the hydrocarbon could be purified by VPC on a 6 ft × 0.25 in. 5% SE-30 on Chromosorb P column at 125 °C: ν_{max} (neat) 3012, 2849, 2770, 1639, 1590, 990, 901, 738, and 713 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 6.7–6.1 (4 lines, H_X), 5.9–5.5 (m, 5), 5.5–4.9 (8 lines, H_A and H_B, J_{AX} = 10, J_{BX} = 18, J_{AB} = 1.5 Hz), 4.1–3.5 (br m, 4).

Dicarbomethoxybenzotriquinacene (12). A mixture of 5.4 g (34.6 mmol) of **11** and 10 g (0.0735 mol) of dimethyl acetylenedicarboxylate was heated at 90 °C under a nitrogen atmosphere for 15 h. The unreacted dimethyl acetylenedicarboxylate was removed from the reaction mixture by distillation at 2 mm pressure (bp 60–65 °C). The resulting viscous liquid was dissolved in 10 ml of 30% ether in pentane to allow crystallization of the adduct. This solid was washed with pentane and dried to yield 9.2 g (89%) of product: δ_{Me_4Si} ($CDCl_3$) 5.83–5.40 (m, 4), 5.40–5.16 (m, 1), 3.94–3.44 (m, 4), 3.80 (s, 3), 3.71 (s, 3), and 2.95 (br s, 3).

A solution of the adduct in 150 ml of dry benzene was treated with 14.0 g of dichlorodicyano-*o*-benzoquinone. After 10 min, the initial deep red solution turned orange and a solid began to deposit. After being stirred at 25 °C for 20 h, the reaction mixture was evaporated and the solid residue was chromatographed on alumina. Elution with ether gave 5.7 g (64%) of **12** which crystallized as colorless needles: mp 88.5–89.5 °C from ethyl ether; ν_{max} (KBr) 2910, 2850, 1720, 1430, 1275, and 1135 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 7.72–7.10 (AB m, J_{AB} = 8.0 Hz, 2), 5.62 (s, 4), 4.58–4.10 (m, 2), 4.10–3.58 (m, 2), 3.87 (s, 3), and 3.79 (s, 3).

Anal. Calcd for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44. Found: C, 72.79; H, 5.58.

Benzotriquinacene (13). Diester **12** (4.0 g, 13.5 mmol) was added to an aqueous solution containing 4 equiv of sodium hydroxide and the suspension was stirred at 40 °C until a homogeneous solution was obtained. Subsequent acidification with 10% hydrochloric acid deposited a white solid which was collected by filtration and dried under vacuum at room temperature. The diacid, which amounted to 3.40 g (94%), was recrystallized from 10% dichloromethan in ether to give white crystals: mp 176–178 °C dec; δ_{max} (KBr) 3600–2300, 1700, 1580, 1480, 1420, 1280, 1180, and 1140 cm^{-1}; δ_{Me_4Si} (CD_3COCD_3) 8.72 (br s, 2), 7.75–7.35 (AB m, J_{AB} = 8.0 Hz, 2), 5.70 (s, 4), and 4.72–3.67 (m, 4).

The dicarboxylic acid (2.0 g, 7.46 mmol) was dissolved in 100 ml of freshly distilled quinoline and placed in a 250-ml three-necked flask equipped with nitrogen gas inlet, condenser, and mechanical stirrer. To the solution was added 4.74 g (74.6 mg-atoms) of copper powder and the mixture was refluxed for 24 h under a nitrogen atmosphere.[21] After this time, the reaction mixture, which had gradually turned black, was cooled to room temperature, diluted with 300 ml of pentane, and decanted from the solid copper residue into a separatory funnel. The pentane solution was thoroughly washed with 2 N hydrochloric acid, water, and saturated sodium bicarbonate solution, before drying and evaporation of solvent. The dark residue was chromatographed on acidic alumina (pentane elution) to give 0.72 g (54%) of **13** as a colorless oil: ν_{max} (neat) 3050, 2980, 1480, 1455, 910, 900, 865, 805, and 725 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 7.12 (s, 4), 5.67 (s, 4), and 4.47–3.73 (m, 4); *m/e* calcd 180.0938, obsd 180.0942.

Anal. Calcd for $C_{14}H_{12}$: C, 93.29; H, 6.71. Found: C, 93.14; H, 6.77.

Photoisomerization of Benzotriquinacene (13). A solution of **13** (0.241 g, 1.34 mmol) in 300 ml of 5% acetone in benzene was irradiated through Corex as predescribed. Progress of the reaction was monitored by VPC (10 ft × 0.125 in. 5% SE-30 on Chromosorb W, 155 °C). After 90 h, 4% of unreacted starting material remained and 8.5% of a single volatile photoproduct had been formed. The solvent was removed by evaporation and the residue was chromatographed through a Florisil column using pentane as the eluent. After concentration of the resulting clear solution, photoproduct **14** was isolated by preparative VPC (12 ft × 0.25 in. 15% SE-30 on Chromosorb G, 160 °C): ν_{max} (neat) 3050, 2960, 1465, 1245, 1085, 945, and 740 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 7.01 (s, 4 H), 3.32 (br s, 3), 2.32–2.26 (m, 4), and 1.70–1.47 (m, 1); ^{13}C NMR ($CDCl_3$) 142.2, 126.0, 121.6, 65.0, 60.1, 42.7, 29.4, and 24.3 ppm; *m/e* calcd 180.0939, obsd 180.0942.

Anal. Calcd for $C_{14}H_{12}$: C, 93.29; H, 6.71. Found: C, 93.16; H, 6.68.

Acknowledgment. The authors are indebted to the National Science Foundation for partial financial support.

Registry No.—2, 31678-74-7; **3,** 60803-88-5; **4,** 54107-02-7; **5,** 60803-89-6; **6,** 60803-90-9; **7,** 58913-91-0; **8,** 60803-91-0; **9,** 60828-34-4; **10,** 60803-92-1; **11,** 60803-93-2; **12,** 60803-94-3; **12** dihydro derivative, 60803-95-4; **12** free acid, 60803-96-5; **13,** 60803-97-6; **14,** 60840-54-2; vinyl chloride, 75-01-4; dimethyl acetylenedicarboxylate, 762-42-5.

References and Notes

(1) (a) National Institutes of Health Postdoctoral Fellow, 1974–1975; (b) National Institutes of Health Postdoctoral Fellow, 1975–1976; (c) National Science Foundation Graduate Fellow, 1972–1975.

(2) S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, **73**, 531 (1973).

(3) H. Hart and M. Kuzuya, *J. Am. Chem. Soc.*, **96**, 3709 (1974); **97**, 2450, 2459 (1975).

(4) A. A. Gorman and J. B. Sheridan, *Tetrahedron Lett.*, 2569 (1969); A. R. Brember, A. A. Gorman, and J. B. Sheridan, *ibid.*, 481 (1973).

(5) G. Kaupp and K. Krieger, *Angew. Chem.*, **84**, 719 (1972); *Angew. Chem., Int. Ed. Engl.*, **11**, 719 (1972).

(6) P. K. Freeman and T. D. Ziebarth, *J. Org. Chem.*, **38**, 3635 (1973).

(7) G. Linstrumelle, *Tetrahedron Lett.*, 85 (1970).

(8) L. A. Paquette, W. B. Farnham, and S. V. Ley, *J. Am. Chem. Soc.*, **97**, 7273 (1975).

(9) M. J. Wyvratt and L. A. Paquette, *Tetrahedron Lett.*, 2433 (1974).

(10) L. A. Paquette, H. C. Berk, C. R. Degenhardt, and G. D. Ewing, to be submitted.

(11) When **8** is redrawn as **ii**, the molecule is seen to be closely related structurally to cuneane (**i**)[12] and norsnoutane (**iii**).[13] To circumvent potential


i


ii


iii

problems with such trivial nomenclature, we offer at this time the suggestion that only **8** and not its isomer **iii** be referred to as "homocuneane".

(12) L. Cassar, P. E. Eaton, and J. Halpern, *J. Am. Chem. Soc.*, **92**, 6366 (1970).

(13) L. A. Paquette and J. C. Stowell, *J. Am. Chem. Soc.*, **92**, 2584 (1970); **93**, 2459 (1971); L. A. Paquette, R. A. Boggs, and J. S. Ward, *ibid.*, **97**, 1118 (1975).

(14) L. A. Paquette, W. P. Melega, and J. D. Kramer, *Tetrahedron Lett.*, 4033 (1976).

(15) R. C. Kelly, Ph.D. Thesis, Harvard University, 1965; L. A. Paquette, G. V. Meehan, and S. J. Marshall, *J. Am. Chem. Soc.*, **91**, 6779 (1969); R. Russo, Y. Lambert, and P. Deslongchamps, *Can. J. Chem.*, **49**, 531 (1971); L. A. Paquette, I. Itoh, and W. B. Farnham, *J. Am. Chem. Soc.*, **97**, 7280 (1975).

(16) R. B. Woodward, T. Fukunaga, and R. C. Kelly, *J. Am. Chem. Soc.*, **86**, 3164 (1964).

(17) D. Bosse and A. de Meijere, *Angew. Chem.*, **86**, 706 (1974); *Angew. Chem., Int. Ed. Engl.*, **13**, 663 (1974).

(18) L. T. Scott and M. Jones, Jr., *Chem. Rev.*, **72**, 181 (1972).

(19) R. Srinivasan, *J. Am. Chem. Soc.*, **92**, 7542 (1970).

(20) S. D. Rosenberg, J. J. Walburn, T. D. Stankovich, A. E. Balint, and H. E. Ramsden, *J. Org. Chem.*, **22**, 1200 (1957).

(21) J. H. Dopper and H. Wynberg, *J. Org. Chem.*, **40**, 1957 (1975).