Photolysis of 6-Methyl-1,2,3,4,5-pentaphenyl-1,3-cyclohexadiene. Crystal Structure of 7-Methyl-2,3,5,6-tetraphenyltricyclo[6.4.0.$0^{4,8}$]dodeca-3,5,9,11-tetraene

Neil F. Woolsey,* Lewis J. Radonovich,* Fathi M. Saad, and Franklin J. Koch

Department of Chemistry, University of North Dakota, Grand Forks, North Dakota 58202

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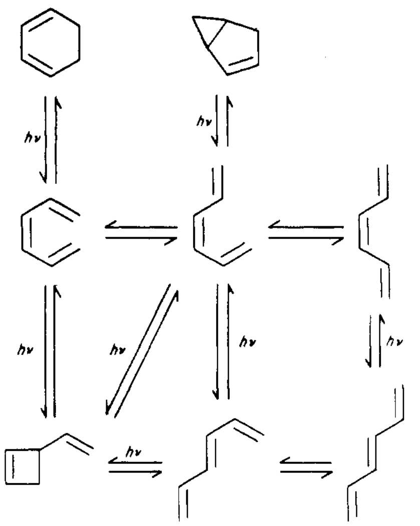
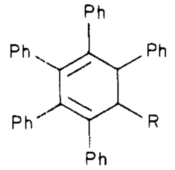
Photolysis of 6-methyl-1,2,3,4,5-pentaphenyl-1,3-cyclohexadiene (**1b**) gave up to 46% of 1,2,3,4,5-pentaphenyl-1,3,5-heptatriene (**5**) and up to 17% of the polycyclic photoproduct 7-methyl-2,3,5,6-tetraphenyltricyclo[6.4.0.$0^{4,8}$]dodeca-3,5,9,11-tetraene (**7**). The structure of the latter was investigated by formation of di- and tetrahydro derivatives and a Diels–Alder adduct. The structure **7** was established by an X-ray structure determination.

The photochemistry of cyclohexadienes and the resulting open-chain triene has been extensively investigated. The classic studies of the vitamin D series have been extended both to other natural products and to synthetic models.[1,2] The current unifying mechanistic model, based on conformational steric and electronic effects, is summarized in Chart I.[2,3] The concept is that different photochemical reactions come from different conformational preferences of the triene initially formed on ring opening. These conformational equilibria in turn are controlled by steric factors.

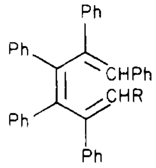
Chart I



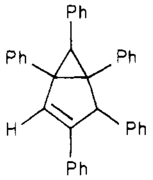
Our studies in this area were initiated before most of the detailed work supporting the above mechanisms was available and were prompted by the report that 1,2,3,4,5-pentaphenylcyclohexadiene (**1a**) gave high yields of the bicyclo[3.1.0]hexene **3**.[4] We wanted to investigate the stereochemistry of this ring closure and the possibility that the bicyclization came directly from the cyclohexadiene. As the chemistry of our probe, *trans*-6-methyl-1,2,3,4,5-pentaphenylcyclohexadiene (**1b**), unfolded, others more adequately answered these questions. The chemistry of **1b**, however, was not the same as that of **1a** or the many other models used in this series.[1] A new reaction manifold was discovered for 3-phenylhexatrienes, namely, an intramolecular [2 + 6] cycloaddition reaction.



1a, R = H
b, R = CH_3



2a, R = H
b, R = CH_3



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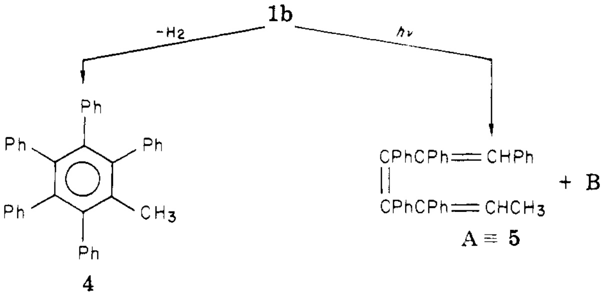
We report here the structures of products isolated from photolysis of **1b** and in one case confirmation of that structure by a single-crystal X-ray diffraction study of the most novel of these. The results are analyzed in terms of the general mechanism postulated elsewhere.

Results and Discussion

trans-6-Methyl-1,2,3,4,5-pentaphenyl-1,3-cyclohexadiene (**1b**) was prepared by the Diels–Alder reaction of (*E*)-1-phenylpropene and tetraphenylcyclopentadienone (tetracyclone).[5] The physical properties were consistent with the assigned structure (see Experimental Section). Dehydrogenation of **1b** gave rise to pentaphenyltoluene (**4**), identified by comparison with an authentic sample prepared by Diels–Alder reaction of 1-phenylpropyne and tetracyclone. Attempts to prepare the corresponding *cis*-**1b** isomer from (*Z*)-1-phenylpropene and tetracyclone resulted only in formation of **4**. This result strongly supported the assigned trans stereochemistry of **1b** since any isomerization of either (*E*)-1-phenylpropene or the product **1b** would have resulted in formation of **4**, which was not found.



4

The trans-cyclohexadiene **1b** was irradiated under a variety of conditions (see Experimental Section). In each case, however, only two photoproducts could be isolated. The first photoproduct, A, assigned structure **5**, was separated in 25–46% yield by crystallization of the crude

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(1) E. Havinga, R. J. Dekock, and M. P. Rappoldt, *Tetrahedron*, **11**, 276 (1960); E. Havinga and J. L. M. A. Shlatmann, *ibid.*, **16**, 146 (1961); G. M. Sanders and E. Havinga, *Recl. Trav. Chim. Pays-Bas*, **83**, 665 (1964).

(2) W. G. Dauben, M. S. Kellogg, J. I. Seeman, N. D. Vietmeyer, and P. H. Wendschuh, *Pure Appl. Chem.*, **33**, 197 (1973); P. J. Vroegop, J. Lugtenburg, and E. Havinga, *Tetrahedron*, **29**, 1393 (1973).

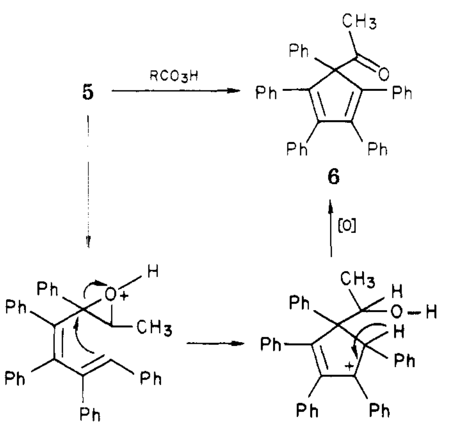
(3) For recent applications of these principles cf. J. W. J. Gielen, H. J. C. Jacobs, and E. Havinga, *Tetrahedron Lett.*, 3751 (1976), and P. Courtot and R. Rumin, *Tetrahedron*, **32**, 441 (1976).

(4) G. R. Evanga, W. Bergmann, and J. English, Jr., *J. Org. Chem.*, **27**, 13 (1962).

(5) C. F. H. Allen, *Chem. Rev.*, **62**, 653 (1962).

0022-3263/79/1944-2483$01.00/0

Chart II



reaction mixture from hexane. The second photoproduct, B, assigned structure **7**, was separated by fractional crystallization in 5–15% yield.

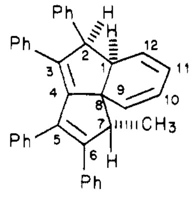
Photoproduct A was assigned structure **5**, an open-chain isomer of **1b**, based on the following data. The IR spectrum showed a band at 840 cm^{-1} which was attributed to the C–H bending mode of the terminal trisubstituted alkene.[6] The ^{1}H NMR spectrum confirmed this assignment by the presence of a vinyl methyl group (δ 1.60, d, $J = 7$ Hz) coupled to a vinyl proton (δ 5.93, q, $J = 7$ Hz). The other terminal vinyl proton of **5** absorbed under the aryl proton multiplet which integrated for 26 protons. The ^{13}C NMR spectrum showed only one aliphatic carbon at 15.7 ppm, assigned to the methyl carbon. The UV spectrum of **5** was abnormal for an open-chain triene, absorbing at 255 nm (ϵ 28 600) with a shoulder at 326 nm (ϵ 13 300). (*E*,*E*)-Phenylhexatriene absorbs at 311 nm (ϵ 55 000).[7] The high steric hindrance of the phenyl rings in **5**, however, would be expected to considerably alter this basic chromophore. Molecular models indicate the likely possibility that in the equilibrium conformation of **5** the chain double bonds are essentially orthogonal and that the major absorbing chromophores are stilbene in nature.

The basic chain structure of **5** was consistent with its cyclization and dehydrogenation with chloranil to pentaphenyltoluene in 52% yield.

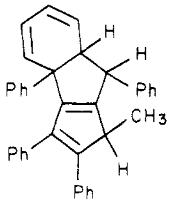
When **5** was treated with 3-chloroperbenzoic acid, a complex mixture resulted from which **6** was isolated in 7% yield. The methyl ketone portion of this structure was supported by an IR carbonyl absorption at 1705 cm^{-1} and a methyl singlet in the NMR spectrum of δ 2.30. The mass spectrum of **6** showed a parent ion at *m/e* 488 with M + 1 and M + 2 ion intensities consistent with the molecular formula $C_{37}H_{28}O$. The ultraviolet spectrum showed a maximum at 340 nm (ϵ 10 000) with a shoulder at 247 nm (ϵ 24 600) which is consistent with a sterically hindered tetraphenylcyclopentadiene chromophore. 1,2,3,4,5,5-Hexaphenylcyclopentadiene absorbs at 247 (ϵ 27 000) and 335 nm (ϵ 13 000).[8]

Formation of the dienone **6** from the triene **5** can be rationalized as shown in Chart II. Epoxidation of the most electron-rich double bond followed by acid-catalyzed opening of the epoxide with concomitant cyclization would give a cyclopentadienol. Further oxidation by peracid during the extended reaction period could result in the formation of the observed dienone **6**. Isolation of this product is thus consistent with the structure **5** assigned to A.

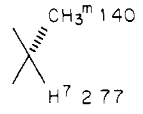
Turning to the structure of the second isomeric photoproduct B, the following evidence supported structure **7** although structure **8** initially appeared possible. The ^{1}H NMR spectrum showed the presence of two isolated groupings C and D with the ^{1}H NMR assignments shown.



7

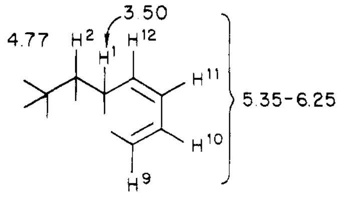


8



$J_{m,7} = 7$ Hz

C

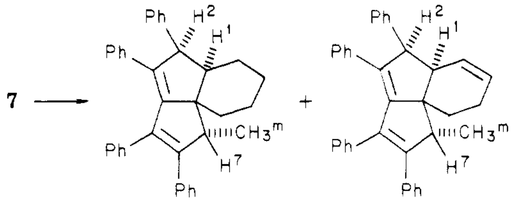


$J_{1,2} = 9$ Hz

$J_{1,12} = 5$ Hz

D

The coupling constant $J_{1,2}$ is consistent with a cis orientation of the hydrogens on a five-membered ring based on the ^{1}H NMR absorptions of substituted indans.[9] The cyclohexadiene moiety was established definitively by formation of a Diels–Alder adduct with maleic anhydride. Catalytic reduction of B gave two products, the physical properties of which were consistent with di- and tetrahydro derivatives of **7**. That only the cyclohexadiene ring had been reduced was established by the ^{1}H NMR spectrum since only the vinyl protons H_{9-12} were converted to methylene groups absorbing upfield. Absorptions due to $H_{2,7,m}$ clearly remained unchanged while H_1 moved under the H_7 absorption. Thus, the tetrahydro derivative was assigned structure **9**.



9 **10**

The ^{1}H NMR spectrum of the dihydro derivative also maintained the methyl group structure and chemical shift of $H_{7,m}$ in **7**. Furthermore, H_2 remained unchanged while H_1 changed multiplicity (now a broad doublet) but did not change position, indicating its vinylogous position had been maintained. These data are consistent with structure **10** for the dihydro derivative.

Comparison of the UV spectra of **7**, **9**, and **10** showed a λ_{max} at 312–313 nm with a molar absorptivity of 18 000–22 000 for all three compounds. Thus, the cyclohexadiene ring was not conjugated with the other unsaturation; otherwise a shift in UV absorption would have been seen. Further, a point by point subtraction of the UV spectrum of **9** from **7** gave a difference spectrum having a λ_{max} of 256 (ϵ 12 000) compared to a λ_{max} of 256

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[6] R. T. Conley, "Infrared Spectroscopy", Allyn and Bacon, Boston, MA, 1966, p 101.

[7] H. C. Barany, E. A. Braude, and J. A. Coles, *J. Chem. Soc.*, 2093 (1951).

[8] A. K. Youssef and M. A. Ogliaruso, *J. Org. Chem.*, **37**, 2601 (1972).

[9] W. E. Rosen, L. Dorfman, and M. P. Linfield, *J. Org. Chem.*, **29**, 1723 (1964).

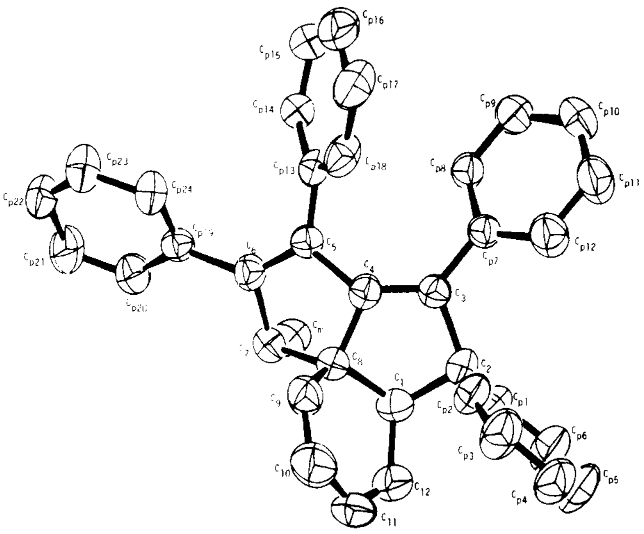
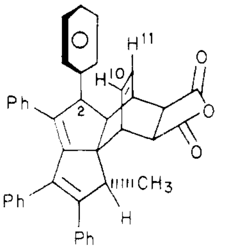


Figure 1. Traced computer drawing of $C_{37}H_{30}$ showing the anisotropic thermal parameters at 50% probability and the atomic numbering scheme.

nm (ϵ 8 000) for 1,3-cyclohexadiene.[10] These data are consistent with destruction of a cyclohexadiene ring on formation of 9 from 7.

The Diels–Alder adduct of 7 has been assigned structure 11. Although the stereochemistry and mode of attack (α or β) are tentative, the indicated α attack forces H_{11} into the phenyl ring at C_2, thus explaining its upfield shift of 0.68 ppm relative to H_{10} in the ^1H NMR spectrum of 11. The endo maleic anhydride orientation was assigned by analogy.

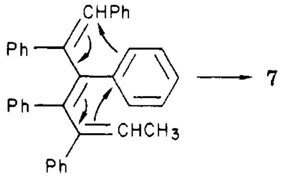


11

Thus, while the detailed chemistry of B supported the features of structure 7 around C_7 and the fused cyclohexadiene ring, these data did not unequivocally establish the tetrahydropentalene portion of the structure. In particular, structure 8 seemed a definite, although less likely, possibility. To settle this point, a complete X-ray structure determination of B was undertaken.

A drawing of one molecule of the compound as it exists in the crystal is shown in Figure 1 with the thermal parameters displayed at 50% probability.[11] The average C–C double bond distance in the five-membered rings is 1.350 (3) Å and the average double bond distance in the cyclohexadiene fragment is 1.321 (4) Å. None of the individual rings within the fused-ring system are planar because of the required sp^3 hybridization of C_1, C_2, C_7, and C_8. Strain at the sp^3 carbons is reflected in the average sp^3–sp^3 bond distance, within the fused-ring system, of 1.564 Å. Nonbonded interactions are normal and are responsible for the observed orientations of the phenyl rings.

Thus, the structure of photoproduct B can unequivocally be assigned as 7. The formation of this new ring system requires some comment. While direct paths from **1b** to 7 can not be eliminated by current data, the most likely mode of formation of 7 is from the major triene photoproduct 5. Initial irradiation of **1b**, based on literature concepts, could give 5. Steric factors probably do not allow further photorearrangement to the bicyclo[3.1.0]hexane or vinyl cyclobutene. Instead the stereochemistry allows a ready [6 + 2] cycloaddition to occur (reaction 1). In



(1)

support of this contention it was found that irradiation of 5 gave yields of 7 similar to those obtained in the irradiation of **1b**. Furthermore, irradiation of 7 gave an 83% yield of 5.

Experimental Section[12]

***trans*-6-Methyl-1,2,3,4,5-pentaphenyl-1,3-cyclohexadiene (1b).** Tetraphenylcyclopentadienone (tetracyclone) (50 g, 0.13 mol) and *trans*-1-phenyl-1-propene (62 g, 0.52 mol) were refluxed in mesitylene (150 mL) for 5 days.[5] The solvent was removed under reduced pressure to give a white solid. After trituration with hexane, the solid was filtered off and washed with hexane. Recrystallization from hexane–ethyl acetate gave the cyclohexadiene **1b** (55 g, 91%): mp 187–187.5 °C; ^1H NMR (CS_2) δ 7.65–6.40 (m, 25 H, aryl), 3.70 (d, 1 H, J = 2 Hz, CHPh), 2.8 (q, J = 2 Hz, J' = 7 Hz, $CHCH_3$), 1.60 (d, 3 H, J' = 7 Hz, CH_3); UV λ_{max} (CH_3CN) 315 (ϵ 11 000), 230 (sh) nm (18 300); IR (Nujol) 1595, 1490, 755, 747, 700 (s) cm^{-1}. Anal. Calcd for $C_{37}H_{30}$: C, 93.62; H, 6.37. Found: C, 93.51; H, 6.40.

This reaction was also carried out on a small scale in a degassed benzene solution sealed in a tube which was heated in a tube furnace at 200 °C for 8 h with similar results.

Pentaphenyltoluene (4). (A) From Tetracyclone and 1-Phenylpropyne. Following the literature procedure,[13] pentaphenyltoluene (4) was prepared in 92% yield; mp (sealed tube) 285–286 °C (lit.[14] mp 284 °C); ^1H NMR ($CDCl_3$) δ 7.15–6.85 (m, 25 H, aryl), 1.93 (s, 3 H, CH_3); UV λ_{max} (CH_3CN) 233 nm (ϵ 45 200).

(B) From Tetracyclone and *cis*-1-Phenyl-1-propene. Tetracyclone (2.00 g, 5.0 mmol), *cis*-1-phenyl-1-propene (1.80 g, 15 mmol) and mesitylene (ca. 10 mL) were sealed in a reaction tube and heated in a tube furnace at 200 °C for 2 days. The solid residue obtained on distillation of the solvent under reduced pressure was recrystallized from hexane–ethyl acetate to give 4 (1.80 g, 78%); mp 279–282 °C (sub). Sublimation gave a pure sample mp 285–286 °C, which was identified by mixture melting point and IR comparison with an authentic sample.

An attempted reaction in refluxing mesitylene for 8 days gave 34% 4 and 50% recovered tetracyclone.

(C) From *trans*-6-Methyl-1,2,3,4,5-pentaphenyl-1,3-cyclohexadiene (1b). A mixture of the cyclohexadiene **1b** (0.50 g, 1.1 mmol), 10% palladium on charcoal (0.10 g), and mesitylene (15 mL) was refluxed for 20 h. The mixture was filtered and the filtrate was cooled in a dry ice–acetone bath and then filtered again to afford starting cyclohexadiene (70 mg, 14%, mp 177–188 °C). Evaporation of the filtrate under reduced pressure gave 4 (0.22 g, 44%); mp 278–280 °C. Sublimation gave a pure sample which

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[10] R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds", Wiley, New York, NY, 1963, p 99.

[11] D. K. Johnson, "ORTEP, a Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations", Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, TN, 1965.

[12] Melting points were determined on a calibrated Fisher-Johns hot stage apparatus. Infrared (IR) and ultraviolet (UV) spectra were recorded on Beckman IR-12 and Cary 14 spectrometers, respectively. Proton NMR spectra were recorded on Varian A 60 and EM 390 spectrometers while carbon-13 spectra were obtained on a JEOL FX-60. All NMR data are reported in parts per million downfield from internal Me_4Si. Mass spectra were recorded by Morgan-Schaffer, Inc., Montreal, Quebec, by T. Kinstle then at Iowa State University, and on a Du Pont CEC-491 spectrometer.

[13] W. Dithey and G. Hurtig, *Chem. Ber.*, **67B**, 2004 (1934).

[14] J. J. Dudkowski and W. I. Becker, *J. Org. Chem.*, 17, 201 (1952).

was identified by mixture melting point and IR comparison with an authentic sample of **4**.

(D) From 1,2,3,4,5-Pentaphenylheptatriene (5). A solution of the triene **5** (0.30 g, 0.63 mmol) and chloranil (1.10 g, 4.5 mmol) in mesitylene (10 mL) was refluxed for 24 h. After solvent removal under reduced pressure, the red solid residue was chromatographed on alumina (32 g). Elution with 3:1 hexane–benzene gave crude pentaphenyltoluene (150 mg, 52%); mp 230–275 °C. A pure sample was prepared by sublimation, mp 285–286 °C, and was identified by mixture melting point and NMR comparison with an authentic sample. Attempted dehydrogenation of the triene with 10% palladium on charcoal in refluxing mesitylene for 96 h gave 80% recovered starting material.

Photolysis of Cyclohexadiene 1b. A solution of the cyclohexadiene **1b** (4.01 g, 8.0 mmol) in redistilled benzene (270 mL) was purged with nitrogen and then irradiated under nitrogen for 35 min.[15] The solvent was removed under reduced pressure and the resulting yellow oil dissolved in a minimum of hexane which deposited white crystals of A (0.65 g, mp 165–167 °C) on standing. Concentration gave a second crop (0.45 g, 165–167 °C, total 27%). Three recrystallizations from hexane–ethyl acetate gave an analytical sample of **5**: mp 167.5–168 °C; ^{1}H NMR (CDCl$_3$) δ 7.70–6.75 (m, 26 H, aryl and PhC**H**), 5.93 (q, 1 H, *J* = 7 Hz, C**H**CH$_3$), 1.60 (d, 3 H, *J* = 7 Hz, CH$_3$); ^{13}C NMR (CDCl$_3$) δ 142.5 (s), 142.3 (s), 141.8 (s), 141.4 (s), 140.7 (s), 137.8 (s), 132.1 (d), 129.1, 128.7, 128.3, 128.0, 127.8, 127.6, 127.2, 127.0, 126.7, 15.7 (q, CH$_3$); UV λ_{max} (CH$_3$CN) 255 (ε 28600), 326 (sh) nm (13000); mass spectrum (70 ev) *m/e* (relative intensity over 1) 474 (0.5, M$^+$), 168 (2), 88 (5), 79 (9), 78 (100), 77 (22). Anal. Calcd for C$_{37}$H$_{30}$: C, 93.63; H, 6.37. Found: C, 93.64; H, 6.36.

Evaporation of the mother liquor gave an oil which was again taken up in a minimum of *n*-hexane and allowed to evaporate slowly at room temperature. A total of 0.45 g (11%), mp 170–175 °C, of B in two crops was obtained. Chromatography of this material on 75 g of silica gel–silver nitrate gave on elution with 7:1 and 4:1 *n*-hexane–benzene 0.35 g of **7**; mp 175–176 °C. Recrystallization further from *n*-hexane did not increase the melting point; mixture melting point with starting material was depressed: mp 155–170 °C; ^{1}H NMR δ 7.5–6.8 (m, 20 H, aryl), 6.20–5.35 (m, 4 H, vinyl), 4.77 (d, 1 H, *J* = 9 Hz, benzylic), 3.5 (q, 1 H, *J* = 9 Hz, *J''* = 5 Hz, methine), 2.77 (q, 1 H, *J'''* = 7 Hz, methine), 1.30 (d, 3 H, *J'''* = 7 Hz, methyl); ^{13}C NMR δ 154.9 (s), 152.5 (s), 141.5 (s), 137.7, 136.2 (s), 136.1 (d), 134.1 (d), 133.9 (d), 132.6 (d, *J* = 163.9 Hz, alkene), 130.2 (d), 129.8 (d), 129.4 (d), 128.4 (d), 128.3 (d), 128.0 (d), 127.9 (d), 127.4 (d), 127.1 (d), 126.8 (d), 126.1 (d), 125.9 (d), 124.1 (d, *J* = 160.2 Hz, alkene), 121.6 (dd, *J* = 160.9, *J'* = 9.2 Hz, alkene), 68.9 (d, *J* = 129.0 Hz, C$_2$), 62.5 (s, C$_8$), 52.5 (d, *J* = 135.1 Hz, C$_7$), 41.3 (dd, *J* = 129.0, *J'* = 7.0 Hz, C$_1$), 16.1 (q, *J* = 126.8 Hz, CH$_3$); UV λ_{max} (CH$_3$CH) 313 (ε 18900), 272 (sh) (ε 17900), 267 (sh) (ε 19000), 262 (sh) (ε 21000), 255 (sh) nm (ε 21600); IR (Nujol) 1590, 1490, 1440, 1370, 765 (s), 745 (s), 735, 710 (s), 700 (s), 690 (s) cm^{-1}; mass spectrum parent ion at *m/e* 474. Anal. Calcd for C$_{37}$H$_{30}$: C, 93.63; H, 6.37. Found: C, 93.35; H, 6.57.

Other runs, irradiating in ether or benzene for 10–60 min, gave yields ranging from 22 to 46% of the triene **5**, with **7** ranging from 8 to 15% under these conditions.

5-Acetyl-1,2,3,4,5-pentaphenyl-1,3-cyclopentadiene (6). To an ice-cooled, stirred, chloroform (30 mL) solution of the triene **5** (1.01 g, 2.13 mmol) was added a solution of *m*-chloroperbenzoic acid (0.995 g, 4.67 mmol, 81% active oxygen) in chloroform (20 mL) over 10 min. After 72 h at room temperature 3.85 mmol of peracid had been consumed (addition of excess potassium iodide followed by standard sodium thiosulfate titration). The white precipitated *m*-chlorobenzoic acid (300 mg, mp 153–155 °C) was filtered off and the filtrate washed twice with 10% sodium carbonate solution and once with water and then dried (MgSO$_4$), and the solvent was removed under reduced pressure. Chromatography on silica gel gave an unidentified pale yellow solid (50 mg, mp 251–253 °C, eluted with 3:1 hexane–benzene) and the crude ketone **6** (mp 198–207 °C, eluted with 1:3 hexane–benzene). Recrystallization from ethanol gave the ketone **6** (70 mg, 7%); mp 205–207 °C. Recrystallization gave an analytical sample: mp 206–208 °C; ^{1}H NMR (CDCl$_3$) δ 7.6–6.8 (m, 25 H, aryl), 2.27 (s, 3 H, COCH$_3$); UV λ_{max} (CH$_3$CN) 340 (ε 10000), 265 (sh) (18000), 247 nm (24600); IR (CHCl$_3$) 1701 (s, CO), 1600 (m), 1493 (s), 1447 (m), 1351 (m), 1156 (m), 1070 (m), 1026 (m) cm^{-1}; mass spectrum (70 ev) *m/e* (relative intensity over 25) 488 (32, M$^+$), 447 (27), 446 (72), 354 (45), 278 (57), 277 (46), 262 (27), 186 (29), 183 (28), 168 (29), 141 (45), 128 (25), 115 (52), 78 (49), 77 (99), 65 (26), 63 (27), 62 (31), 57 (26), 55 (29), 51 (70), 43 (89), 41 (49), 39 (58), 28 (100), 27 (60). Anal. Calcd for C$_{37}$H$_{28}$O: C, 90.95; H, 5.78; O, 3.27. Found: C, 91.05; H, 5.94; O, 3.00.

Hydrogenation of 7. A solution of **7** (0.09 g, 1.9 mmol) in 80 mL of ethyl acetate and 10% palladium on charcoal (0.20 g) was treated with 40 psi starting pressure of hydrogen gas for 2 h in a Parr hydrogenation apparatus. The catalyst was filtered off and the filtrate evaporated to a yellow solid under reduced pressure. TLC showed no starting material and two overlapped spots. The hydrogenated product from 1.23 g of **7** treated as above was chromatographed on 100 g of silica gel–silver nitrate. Fraction A, eluted with 4:1 hexane–benzene (500 mL), afforded 0.60 g (48%) of the tetrahydro derivative **9**; mp 170–173 °C. Recrystallization three times from hexane and drying over silica gel–paraffin wax for 3 days at 100 °C (0.3 mm) gave an analytical sample: mp 171–172 °C; ^{1}H NMR δ 7.6–6.8 (m, 20 H, aryl), 4.67 (d, 1 H, *J* ≈ 9 Hz, PhCH), 3.15–2.67 (br q, 2 H, *J'* = 7 Hz, CH), 2.1–2.85 (br m, 8 H, cyclohexane CH$_2$); UV λ_{max} (CH$_3$CN) 312 nm (ε 20400); IR (Nujol) 1600, 1495, 1080, 1030, 910, 780, 770, 760, 540 (m) cm^{-1}; mass spectrum parent ion peak at *m/e* 478 with a strong peak at *m/e* 476. Anal. Calcd for C$_{37}$H$_{34}$: C, 92.84; H, 7.16. Found: C, 92.71; H, 7.02.

Fraction B, eluted with 1:1 hexane–benzene (200 mL), gave (isolated as above) 0.35 g (28%) of the dihydro derivative **10**; mp 193–195 °C. Recrystallization three times and drying as above gave an analytical sample: mp 192.5–193.5 °C; ^{1}H NMR δ 7.35–6.77 (m, 20 H, aryl), 5.7 (br s, 2 H, *J''* = 2 Hz, vinyl), 4.85 (d, 1 H, *J* ≈ 9 Hz, PhC**H**), 3.35 (br d, 1 H, *J* = 10 Hz, CH), 2.75 (q, 1 H, *J'* = 7 Hz CH), 1.9 (asym s, 4 H, *J''* = 2 Hz, CH$_2$), 1.23 (d, 3 H, *J'* = 7 Hz, CH$_3$); UV λ_{max} (CH$_3$CN) 312 nm (ε 22000); IR (Nujol) 1605, 1500 (s), 1490, 1450, 1080, 1035, 915, 800, 780 (s), 765, 755 (s), 730 (s), 700 (s), 540 cm^{-1}. Anal. Calcd for C$_{37}$H$_{32}$: C, 93.23; H, 6.77. Found: C, 93.23; H, 6.98.

Maleic Anhydride Adduct 11. A solution of **7** (0.10 g, 0.21 mmol), maleic anhydride (28 mg, 0.28 mmol), and 0.31 mL of tetrachloroethylene was degassed and sealed in an NMR tube. The mixture was heated for 70 h in a tube furnace at 160–165 °C after which time the ^{1}H NMR spectrum showed the disappearance of two of the original vinyl protons. The tube was opened and the white precipitate of the adduct **11** filtered off (0.12 g 100%); mp 260–265 °C. Recrystallization from methanol–chloroform afforded white platelets: mp 261–262 °C (after drying); ^{1}H NMR δ 7.5–6.65 (m, 20 H, aryl), 6.35 (br t, 1 H, *J* = 7 Hz, =CH^{10}), 5.67 (br t, 1 H, *J* = 7 Hz, =CH^{11}), 5.06 (d, 1 H, *J'* ≃ 10 Hz, PhCH$_2$), 3.7–3.4 (m, 2 H, methine), 3.2–2.7 (m, 4 H, methine), 1.35 (d, 3 H, *J* = 7 Hz, CH$_3$); UV λ_{max} (CH$_3$CN) 319 (ε 17600), 235 (11000), 220 (sh) nm (19200); IR (Nujol) 1860 (w) and 1775 (s, anhydride), 1235–1225 (m, doublet), 950, 910 (s), 770, 700, 690 cm^{-1}; the mass spectrum showed a parent ion at *m/e* 572. Anal. Calcd for C$_{41}$H$_{32}$O$_3$: C, 85.68; H, 5.78. Found: C, 85.53; H, 5.93.

Irradiation of Heptatriene 5. A solution of the triene **5** (0.05 g, 1.1 mmol) in 270 mL of benzene was purged with nitrogen in Pyrex and irradiated for 35 min. Removal of solvent and repeated crystallization from *n*-hexane gave first the starting triene **5** (200 mg, 40%), mp 167–168 °C, followed by **7** (50 mg, 10%), mp 174–175 °C. Both compounds were identified by a mixture melting point with authentic material.

Irradiation of the Tricyclotetraene 7. A solution of **7** (100 mg, 0.21 mmol) in 0.2 mL of hexadeuteriobenzene was placed in a Pyrex NMR tube, degassed, and sealed under vacuum and then irradiated for 110 min. The solvent was removed and the residue

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[15] Irradiations were carried out with a Hanovia 550- or 450-W medium-pressure mercury lamp in a Pyrex reaction vessel equipped with a Pyrex, water-cooled immersion well, a nitrogen inlet, and a magnetic stirrer. Both benzene and ether were employed as solvents with comparable results; however, the size of the run seemed to affect the yields considerably. A few preliminary runs were conducted on a small scale with quartz apparatus by irradiating an ether solution of **1b** with a low-pressure mercury arc. A low yield of the photoproduct **7** was isolated but no **5** could be detected by ^{1}H NMR. This result is consistent with wavelength dependence of other triene irradiations.[3]

was crystallized from *n*-hexane and then recrystallized from *n*-hexane–ethyl acetate to give the heptatriene **5** (50 mg, 50%); mp 166–167 °C. Concentration of the filtrate gave starting **7** (40 mg, 40%), mp 174–175 °C, from *n*-hexane. Both compounds gave satisfactory mixture melting points.

X-Ray Structure of Photoproduct B. Colorless crystals of tricyclophotoproduct **7** were grown from a hexane solution. The crystal selected for structure analysis was a parallelepiped with approximate dimensions 0.30 × 0.23 × 0.23 mm and was mounted on a glass fiber with silicone adhesive. Precession photographs of this crystal led to a space group assignment of $P2_1/c$ with lattice constants of $a = 14.813\ (2)$ Å, $b = 10.717\ (2)$ Å, $c = 16.827\ (3)$ Å, and $\beta = 80.84\ (2)°$. The observed and calculated densities, assuming four molecules of $C_{37}H_{30}$ per unit cell volume, were 1.18 g/mL.

Data were collected on a Picker FACS 1 diffractometer by using the θ–2θ scan technique with Zr-filtered Mo Kα radiation and a takeoff angle of ~2.5°. Each of the 3774 independent data ($2\theta \leq 45.77°$) was scanned 1.2° in 2θ plus an allowance for spectral dispersion at a rate of 1°/min, and backgrounds were of 20-s duration. Three standards inserted after every 100 reflections remained statistically constant.

The data were reduced to a set of $|F_o|$'s by application of Lorentz and polarization corrections (Lp). Standard deviations were calculated according to

$$\sigma_F = [(C + k^2B)/4|F_o|^2(Lp)^2]^{1/2}$$

where C and B are the counts of scan and backgrounds, respectively, and k is the ratio of scan to background counting time. Some 2897 data with $F_o > 2\sigma_F$ were taken as observed and used in final stages of refinement.

Normalized structure factor amplitudes $|E|$'s were calculated[16] and the largest 400 were used in the reiterative application of the Sayre equation.[17] Carbon atomic positions found from an E map[18] were used in full-matrix isotropic refinement[19,20] followed by block-diagonal anisotropic refinement[21] which produced an R value of 10.7%, where $R = \sum||F_o| - |F_c||/\sum|F_o|$. A Fourier difference synthesis[18] at this stage provided for the 30 H atoms.

In order to reduce the number of varied parameters, theoretical positions of the 20 phenyl hydrogens were calculated at a distance of 0.95 Å from their respective carbons and included as fixed contributors in the subsequent cycles of refinement[21] while the coordinates of the 10 hydrogens in the fused-ring system were varied. This unit-weighted refinement converged with an R value of 6.1% and $R_w = 6.1\%$, where $R_w = \sum[w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$. Empirical weights were then calculated as described previously[22] and used in the final cycles of refinement, which produced $R = 5.76\%$ and $R_w = 5.91\%$.

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Registry No. 1b, 33593-04-3; **4**, 23934-49-8; **5**, 70456-57-4; **6**, 70456-58-5; **7**, 70456-59-6; **9**, 70456-60-9; **10**, 70456-61-0; **11**, 70456-62-1; tetracyclone, 479-33-4; *trans*-1-phenyl-1-propene, 873-66-5; 1-phenylpropyne, 673-32-5; *cis*-1-phenyl-1-propene, 766-90-5; maleic anhydride, 108-31-6; tetrachloroethylene, 127-18-4.

Supplementary Material Available: Tables of bond distances (Table I) and angles (Table II), atomic coordinates (Table III), and thermal parameters (Table IV) for photoproduct **7** (6 pages). Ordering information is given on any current masthead page.

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[16] Program FAME by R. Dewar and A. Stone was used.

[17] Program REL by R. E. Long was used.

[18] Program FORDAP by A. Zalkin was used.

[19] Atomic form factors from D. T. Cromer and J. L. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).

[20] W. R. Busing, K. D. Martin, and H. A. Levy, "OR-FLS, A Fortran Crystallographic Least-Squares Program", Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, TN, 1962.

[21] Program REFINE by J. J. Park was used. The function minimized was $\sum w|F_o| - |F_c|^2$.

[22] L. J. Radonovich, A. Bloom, and J. L. Hoard, *J. Am. Chem. Soc.*, **94**, 2066 (1972).

Synthetic Studies in Unnatural Cyclic Amino Acids

Ving J. Lee*[1a] and R. B. Woodward*[1b]

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

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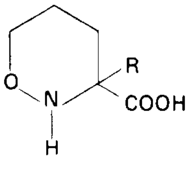
The nitrosation of diethyl (3-chloropropyl)malonate with ethyl nitrite–sodium ethoxide affords ethyl 5,6-dihydro-4*H*-1,2-oxazine-3-carboxylate (**7**), which was converted into 5,6-dihydro-*N*-methyl-4*H*-1,2-oxazine-3-carboxamide (**10**). Chloroacetylation and acetylation of **10** produce dehydro amides **11** and **12**, respectively. These were converted into derivatives of DL-tetrahydro-2*H*-1,2-oxazine-3-carboxylic acid (**1a**).



1a, R=H

1b, R=OCH$_3$

Vast methodology exists in the literature for the synthesis of α-amino acids and their derivatives. However, there is a paucity of information pertaining to the chemistry of unnatural cyclic amino acids, specifically those with a nitrogen–oxygen bond β to the carboxylate function. We were interested in an unambiguous synthesis of DL-tetrahydro-2*H*-1,2-oxazine-3-carboxylic acids (**1a**, R = H; **1b**, R = OCH$_3$) and their derivatives in connection with several synthetic goals. Amino acids **1a**,**b** are of potential utility as biochemical probes as well as synthons

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[1] (a) Please address correspondence to Infectious Disease Research Section, Lederle Laboratories, American Cyanamid Co., Pearl River, New York 10965. (b) Department of Chemistry, Converse Laboratory, Harvard University, Cambridge, Mass. 02138.