Synthesis, Chiroptical Properties, and Absolute Configuration of (+)-2,3-Dihydrotriquinacen-2-one. Effect of Rigid Triquinacene Geometry on the Inherently Dissymmetric Chromophore

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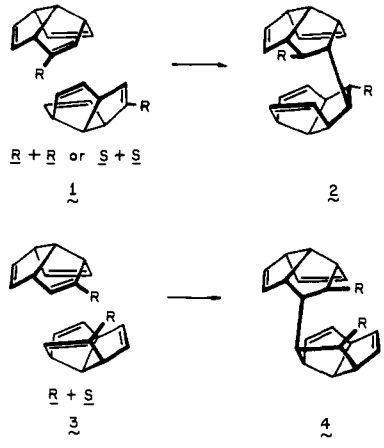
Abstract: Tetracyanoethylene adds to cyclooctatetraeneiron tricarbonyl by a 1,3-bonding scheme to give a σ,π-tetrahapto complex which upon oxidation with ceric ion provides dihydrotetracyanotriquinacene **7** in 94% overall yield. This nitrile is readily hydrolyzed (acidic conditions) to carboxylactone **8a**. By subjecting **8a** sequentially to the action of lead tetraacetate and iodine under photochemical conditions, potassium carbonate in aqueous tetrahydrofuran, and ethereal diazomethane, access is gained to hydroxy ester **10**. Methyl triquinacene-2-carboxylate is produced upon dehydration of **10**. The derived acid is easily resolved as its (+)-(*R*)-α-phenethylamine salt. The (+)-enantiomer of **12b** so obtained, upon treatment with diphenylphosphonic azide (Curtius rearrangement), provides enantiomerically homogeneous (+)-2,3-dihydrotriquinacen-2-one (**16**). Primary determination of optical purity in this series relies upon comparison of relative signal intensities in the ^{1}H NMR spectrum of the (+)-(*R*)-α-phenethylamide of (−)-**12b**. The absolute configurations of (+)-**16** and its tetrahydro derivative, (+)-**25**, are established as (1*S*) by chiroptical measurements of the long wavelength n → π^* transitions. These compounds represent the first members of the triquinacene family for which absolute configurational assignments are available.

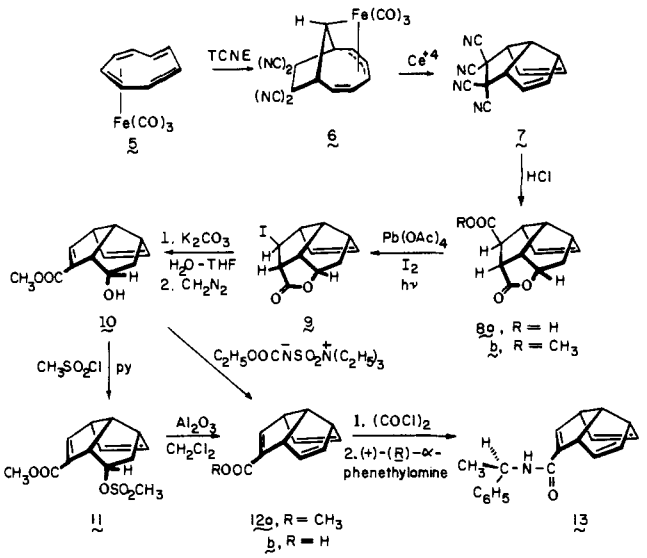
Consideration of the possibility that appendage of an appropriate R group at C_2 of the triquinacene nucleus[2] might serve to direct endo,endo coupling of the monomeric units has promoted special interest in the development of efficient synthetic routes to 2-substituted triquinacenes.[3] The resulting "dimers" assume central importance as a consequence of their obvious suitability for ultimate construction of the dodecahedrane framework. However, there exists an intriguing relationship between the dissymmetry of such derivatized triquinacenes and the structural features inherent in the "dimers". In the hypothetical situation where β,β' bonding operates, it is seen that only when trienes of like configuration are coupled does a molecular array result which is directly relatable to dodecahedrane. This situation is exemplified in the generalized conversion of **1** to **2**. To facilitate visual analysis, **2** has been drawn in one of its stereochemically more encumbered conformations. By contrast, similar controlled dimerization of enantiomeric triquinacene derivatives (e.g., **3**) fails in providing access to a product having the requisite structural features (**4**). Identical subtle factors are at play in the α,α' bonding mode.[4] Because enantiomerically pure 2-substituted triquinacenes are unable to enter into "wrong-way" coupling schemes, the availability of such molecules could permit efficient construction of possible dodecahedrane precursors. In our examination of this question, chiral triquinacene-2-carboxylic acid and 2,3-dihydrotriquinacen-2-one have figured as key compounds. Their ready preparation in optically pure form is detailed herein. Also reported are the first absolute configurational assignments to members of the triquinacene family of compounds.



Synthesis and Resolution of Triquinacene-2-carboxylic Acid. Direct entry to the title acid was conveniently achieved by utilization of the eight constituent carbons of cyclooctatetraene (necessarily reorganized to comprise ultimately C_1, C_4–C_{10}) with incorporation of the tetracyanoethylene moiety (the source of C_2, C_3, and the carboxyl group). The requirements of this molecular construction are met in the reaction of TCNE with cyclooctatetraeneiron tricarbonyl (**5**), the resulting cycloaddition giving rise to the σ,π-Fe(CO)$_3$ complex **6** in 96% yield.[5,6] Confirmation of the stereochemistry of **6** was achieved by three-dimensional x-ray crystal structure analysis.[6] Although this reaction is not new,[7] previous structural assignments to the adduct have been consistently erroneous owing chiefly to its presumed total insolubility in organic solvents. Consequently, detailed spectral information was formerly lacking, and the tetranitrile complex was variously considered to be the result of 1,2- and 1,4-capture of the dienophile. This clearly is not the case, and further examination of this rather unprecedented 1,3-bonding scheme has shown it to be entirely general.[8,9] Oxidative degradation of **6** with ceric ammonium nitrate in 95% ethanol serves to extrude the iron atom with resultant bonding of the apical carbon to the more central π-allyl carbon (Scheme I). Tetranitrile **7**, whose structure has also been ascertained using x ray methods,[6] can be routinely isolated in 98% yield.

Usually, TCNE adducts are recalcitrant to hydrolysis.[10] In this context, the reactivity of **7** is somewhat exceptional, for its conversion to carboxylactone **8** can be effected with hot concentrated hydrochloric acid. This transformation proceeds in 95% yield when effected in sealed glass tubes at 130° for 11 hr. It has proved more convenient for larger scale runs to operate at the reflux temperature of the aqueous acid in open vessels (28 hr). Under such conditions, however, the realized yields are somewhat lower (82%).

Scheme I



Two distinct olefinic protons are observed in the ^{1}H NMR spectrum at δ 5.63 (br d, J = 5.5 Hz) and 5.42 (br d, J = 5.5 Hz). In addition, the >CHOCO- proton appears as a multiplet at 4.85–5.2. The two >CHCO- protons are unfortunately obscured by the other methine protons. Thus, the exo nature of the carboxyl group could not be unequivocally established spectroscopically but is rather inferred on thermodynamic grounds, our inability to achieve double lactonization, and the nonepimerizable nature of derived methyl ester **8b**. Although one of the needed double bonds is lost as the result of intramolecular lactonization, its reconstitution was readily accomplished later in the scheme.

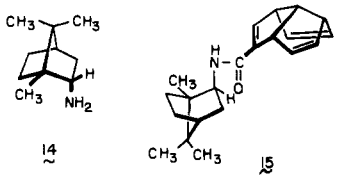
Treatment of **8a** with lead tetraacetate and iodine in carbon tetrachloride–benzene solution (1:1) under conditions of concomitant irradiation from a 250-W tungsten lamp source[11] gave iodolactone **9** in 56% isolated yield. Mild hydrolysis of **9** with potassium carbonate in tetrahydrofuran–water (1:1) at 25° for 32 hr proceeded with simultaneous dehydroiodination. Subsequent direct methylation of the resulting crystalline hydroxy acid with excess diazomethane afforded hydroxy ester **10** as a clear oil showing infrared maxima at 3500 and 1720 cm^{-1}. We have not found it possible to modify conditions so as to achieve iododecarboxylation of **9** with formation of *endo*-2,3-dihydrotriquinacen-2-ol. Presumably, this is a direct consequence of the geometry intrinsic to the intermediate carboxylate anion, attainment of the requisite[12] antiperiplanar arrangement of $-COO^-$ and -I being precluded by the conformational rigidity of the tetrahydrotriquinacene superstructure.

Hydroxy ester **10** could be directly dehydrated with ethyl(carboxysulfamoyl)triethylammonium hydroxide inner salt[13] in dry tetrahydrofuran solution at 25° (56% yield). A somewhat more convenient procedure involved prior conversion of **10** to mesylate **11** and treatment of this derivative with a slurry of neutral activity I alumina in dichloromethane at 25°.[14,15] The ^{1}H NMR spectrum ($CDCl_3$) of **12a** shows a downfield olefinic proton absorption at δ 6.64 (H_3), multiplets of area 4 at 5.5–5.95 and 3.7–4.1, and a three-proton singlet at 3.73. Saponification of **12a** proceeded quantitatively to give **12b**.[16]

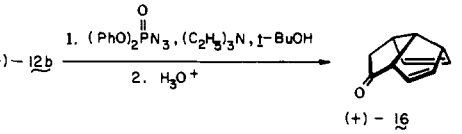
Efficient resolution of this triene carboxylic acid was readily achieved by fractional crystallization of the (+)-(*R*)-α-phenethylamine[17] salts from methanol–water (4:1). The less soluble diastereomer exhibited $[\alpha]^{25}_{365}$ −97.8° (*c* 0.3, ethanol). Acidification of this salt afforded (−)-**12b**, $[\alpha]^{25}$D −12.3°, $[\alpha]^{25}_{365}$ −339° (*c* 0.5, ethanol), which was shown to be enantiomerically pure by conversion to amide **13** through stepwise treatment with oxalyl chloride[18] and (+)-(*R*)-α-phenethylamine in benzene containing pyridine. Whereas the amides prepared from a partially resolved sample of **12b** ($[\alpha]^{25}_{365}$ +13°) exhibited a distinct pair of methyl doublets (C_6D_6, $\Delta\delta$ = 2.7 Hz at 60 MHz; diastereomeric ratio ca. 55:45), pure **13** $[\alpha]^{25}$D −37.0° (*c* 0.7, ethanol) showed only the upfield methyl doublet at δ 1.24. In an unsuccessful attempt to establish the enantiomeric composition of (−)-**12a**, the chiral shift reagent tris(3-trifluoromethylhydroxymethylene)-*d*-camphoratoeuropium(III)[19] did not produce "resonance doubling" of the signals (100 MHz) due either to the methyl group or the downfield shifted olefinic proton H_3.

Enantiomerically homogeneous (−)-**12b** is characterized by a lone electronic absorption maximum at 224 nm (ϵ 6230) and a negative Cotton effect: $[\theta]_{278}$ 0, $[\theta]_{224}$ −79800, $[\theta]_{210}$ 0, $\Gamma/2$ = 20 nm[20] (*c* 0.05, ethanol, 25°).

The possibility of establishing the absolute configuration of (−)-triquinacene-2-carboxylic acid by x-ray crystal structure analysis of amide **13** was investigated, but a solution to the problem has not been realized.[21] When comparable difficulties were encountered with a second amide (**15**) prepared from chiral amine **14**,[22] further work along these lines was discontinued.



Preparation of (+)-2,3-Dihydrotriquinacen-2-one. Modified Curtius rearrangement of (−)-**12b** utilizing a mixture of diphenylphosphonic azide,[23] triethylamine, and *tert*-butyl alcohol conveniently provided enantiomerically pure (+)-**16** ($[\alpha]^{25}$D +450°, $[\alpha]^{25}_{365}$ +2864° (*c* 0.51, ethanol))

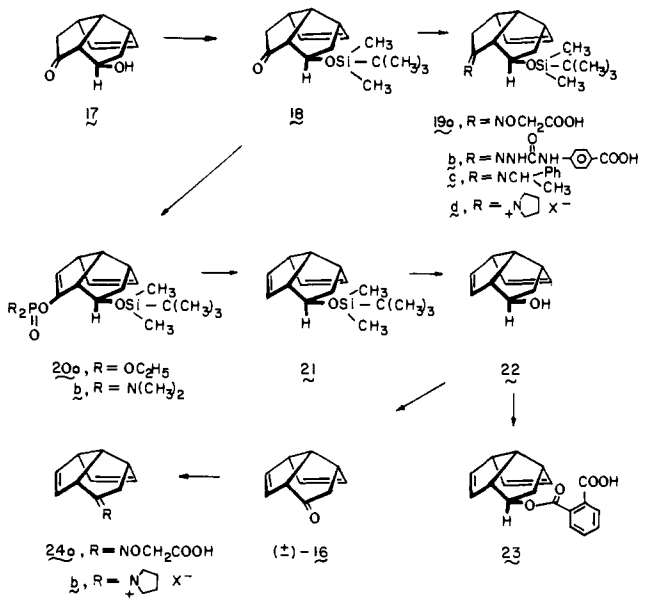


in yields of 46–50%. The spectral properties of chiral **16**[24] correspond to the data previously reported for the racemic ketone.[25]

Because racemic hydroxy ketone **17**[15] can now be prepared in appreciable quantities,[26] the efficient resolution of this compound or a close congener attracted our attention. Direct application of the acid phthalate method failed, chiefly due to considerable decomposition during attempted ester formation and because of the lability of **17** to the alkaline conditions ultimately required for saponification. On the assumption that the β-hydroxyl group was the seat of the difficulty, **17** was converted to **18** by reaction with *tert*-butyldimethylchlorosilane and imidazole in dry dimethylformamide.[27] Notwithstanding, success was lacking in our attempts to resolve **19a–19d** either because the protecting group was removed (in the case of **19a**) or because decomposition was too severe under the range of reaction conditions employed to gain synthetic entry.

Although silyl ether **18** proved not to be amenable to resolution, it has served as a key intermediate in an efficient new synthesis of racemic 2,3-dihydrotriquinacen-2-one (**16**). Thus, conversion to enol diethyl phosphate **20a** or to *N,N,N',N'*-tetramethylphosphorodiamidate (**20b**) proceeded smoothly, and treatment of either derivative with lithium in ammonia[28] at −78° occurred without accompanying overreduction to give **21** in good yields (Scheme II). Exposure

Scheme II



of **21** to tetrabutylammonium fluoride in tetrahydrofuran[27] afforded alcohol **22** (90%), oxidation of which with the chromium trioxide–dipyridine complex gave **16.**

When it was discovered that all of the prepared amine salts of acid phthalate **23** failed to crystallize, two alternative procedures for preparing enantiomerically enriched ketone **16** were investigated. Attention was first given to O-carboxymethoxime **24a** which was available in quantitative yield. Of the chiral amines employed, (+)-(*R*)-α-phenethylamine showed the greatest promise in crystallinity, although the separation of diastereomeric salts did not proceed efficiently. With isopropyl alcohol as solvent, a sample of **24a** ($[\alpha]^{24}_{365}$ +346° (*c* 0.2, ethanol)) was isolated after a number of recrystallizations. Mild acid hydrolysis gave ketone **16** exhibiting $[\alpha]^{24}_{365}$ +1023° (*c* 0.8, ethanol), corresponding to 37% optical purity. Because the losses in material encountered during the fractionation were too high considering the level of resolution achieved, this scheme was not pursued.

The pyrrolidine iminium salt procedure for the resolution of ketones[29] was next attempted. Upon treatment of (+)-**16** with pyrrolidine perchlorate, however, the reaction mixture became very dark and, unlike the reported examples,[29] no crystalline material (e.g., **24b**) was obtained.

In view of these findings, the sole currently available access route to optically pure 2,3-dihydrotriquinacen-2-one (and further transformation products thereof[4]) is seen to be dependent upon the unequalled ready resolvability of triquinacene-2-carboxylic acid.

Chiroptical Properties and Absolute Configuration of (+)-16. The CD curve of (+)-**16** (Figure 1) reveal the sign, shape, and intensity of the Cotton effect of the n → π* transition in the region 260–360 nm. Clearly, the fixed geometry of the β,γ-unsaturated ketone moiety, while unfavorable to an extraordinarily large homoconjugative interaction (vide infra),[30] does allow for transition moment coupling[31] between carbonyl and carbon–carbon π-bond states. Because the n → π* transition is capable of borrowing intensity from the allowed π → π* transition, enhancements of both the extinction coefficient of the 297 nm band (ε 88)[32] and the intrinsic rotatory power result. The chiroptical spectra suggest that (+)-**16** constitutes an inherently dissymmetric chromophore,[33] the homoconjugated double bond (and not the more distant γ,δ double bond[34]) dominating the sign of the long wavelength Cotton effect. In accordance with the modified octant rule proposed for this chromophore,[33,35] the positive Cotton effect of the enhanced n → π* transition in (+)-**16** is consistent with the absolute configurational assignment A. Consequently, the formulas employed in Schemes I and II, and elsewhere in the text, have been drawn accordingly. For convenience, C_1 serves as the point of reference and, on this basis, (+)-**16** may be referred to as the 1*S* enantiomer.

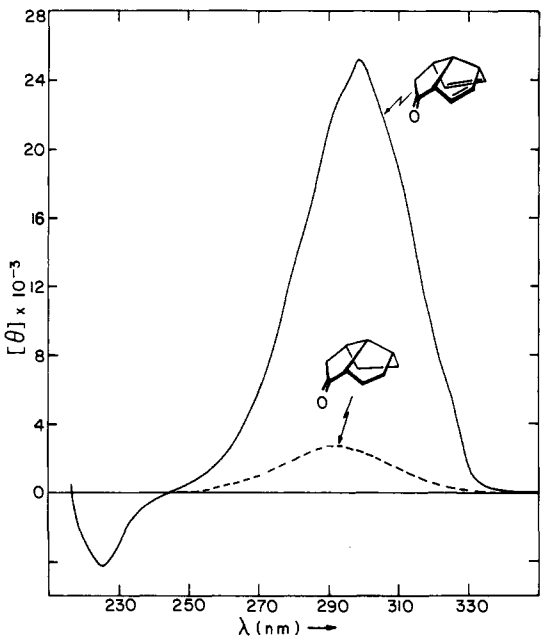
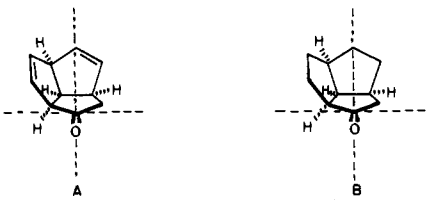


Figure 1. Circular dichroic spectra (ethanol solution) of (+)-2,3-dihydrotriquinacen-2-one (**16,** solid line) and (+)-tricyclo[5.2.1.$0^{4,10}$]decan-2-one (**25,** dotted line).



Corroboratory evidence for this assignment was obtained from the CD spectrum (Figure 1) of (+)-tricyclo-[5.2.1.$0^{4,10}$]decan-2-one (**25**). This optically active saturated ketone[36] was prepared by catalytic reduction of enantiomerically pure (+)-**16** over palladium on carbon. The circular dichroism curve is characterized again by a positive Cotton effect of the n → π* transition for the carbonyl moiety at ca. 290 nm. The contrast between the amplitude of the Cotton effect of (+)-**16** and (+)-**25** is most instructive. This chiroptical behavior is consistent with an octant diagram projection[37] (B) which places the ethano bridge lying closer to the carbonyl group in either an upper left or lower right (+) rear octant.[38] It follows, therefore, that the absolute configuration of (+)-**25** is also 1*S*.[39]

Discussion

As mentioned before, the observed bathochromic shift and enhanced oscillator and rotational strengths of n → π* transitions in β,γ-unsaturated ketones can be understood in terms of coulombic coupling of locally excited states. It was early recognized, however, that this borrowing by the carbonyl n → π* transition of electric dipole transition moment from the ethylenic π → π* transition is intrinsically dependent upon the relative spatial disposition of the carbonyl group and the double bond since electrostatic repul-

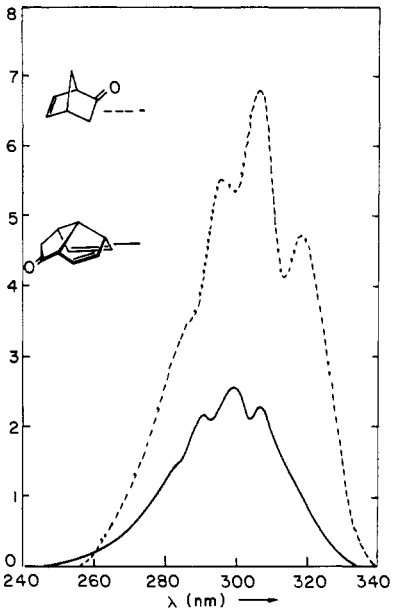


Figure 2. Comparative circular dichroic spectra (isooctane solution) of (+)-**16** (solid line) and (+)-dehydronorcamphor (dashed line). The datum for the latter ketone was taken from D. J. Sandman and K. Mislow, *J. Org. Chem.*, **33**, 2924 (1968).

sion and orbital overlap vary with geometry.[33] Accordingly, the intensities of Cotton effect curves should directly reflect the stereochemical orientation of these functional groups.

The octant diagram for (+)-**16** given by A shows the principal perturbation to be associated with the upper left rear octant and to produce a positive rotation in accordance with the octant rule. That its β,γ-double bond resides in this octant is no doubt the major cause of the much larger positive contribution to ΔE from (+)-**16** relative to its saturated counterpart (+)-**25** (see B). On the other hand, when the rotational strength of the n $\rightarrow$ π^* transition of (+)-**16** is compared, for example, with that of dehydronorcamphor (Figure 2), the $[\theta]_{max}$ for 2,3-dihydrotriquinacen-2-one is seen to be considerably smaller. By use of Mason's relationship[42,43]

$$\log R = \tfrac{1}{2} \log D + C$$

and approximating R by $\Delta\epsilon$ and D by ϵ,[44] relevant comparison can be made of β,γ-unsaturated ketones having otherwise diverse structural features. The plot in Figure 3, where the slope has the theoretical value of 0.5,[43] shows the data fit to be quite good given the assumption that C remains reasonably constant when the orientation of >C=C< and >C=O is not grossly altered.[45]

(+)-25 26

In Figure 3, (+)-2,3-dihydrotriquinacen-2-one clearly occupies an extreme low-end position, the magnitude of its log $(\Delta\epsilon/\epsilon)$ term also falling somewhat below the line. In the latter property, (+)-**16** is seen to parallel the behavior of (+)-3,4,4-trimethylbicyclo[3.2.0]hept-2-en-7-one (**26**).

The difference in $\Delta\epsilon$ between (+)-**16** and (+)-**26** might be accounted for in at least two ways. Firstly, because of the dependence of $\Delta\epsilon$ upon the angle θ (see Figure 3),[34] the inequality of θ in this pair of ketones could be a major cause of the change in magnitude. Also, the γ,δ-double bond in (+)-**16** lies in the upper right rear octant (see A) and therefore makes a negative contribution to the rotational strength of the n $\rightarrow$ π^* transition. Although ketone **26** possesses methyl groups which also provide such opposite contributions, the impact of the π bond in (+)-**16** may be greater.

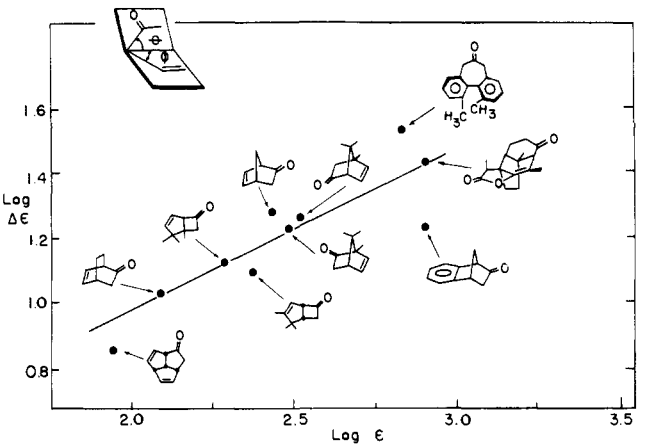


Figure 3. Plot of log $\Delta\epsilon$ for the long wavelength n $\rightarrow$ π^* transitions of several β,γ-unsaturated ketones.

Finally, the observation that (+)-**16** lies close to the line in Figure 3 is consistent with the earlier conclusion that the contribution made by the β,γ-double bond is the dominant chiroptical feature of this triquinane derivative.

Experimental Section

Proton magnetic resonance spectra were recorded with Varian A-60A, Varian HA-100, and Jeolco MH-100 instruments. Apparent splittings are given in all cases. Infrared spectra were recorded on Perkin-Elmer Model 137 and 467 spectrometers, whereas mass spectra were obtained with an AEI-MS9 instrument at an ionizing potential of 70 eV. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Optical rotations were measured with a Perkin-Elmer Model 141 polarimeter and the ORD/CD measurements were taken on a Jasco ORD/UV-5 spectropolarimeter equipped with a CD attachment (Sproul Scientific SS 20-2).

Hydrolysis of 8,8,9,9-Tetracyanotricyclo[5.2.1.0^{4,10}]deca-2,5-diene A. Sealed Tube Conditions. Tetranitrile **7**[5,6] (2.0 g, 8.62 mmol) was heated together with concentrated hydrochloric acid (20 ml) in a thick-walled sealed tube at 130° for 11 hr. The tube was cooled to −77° before opening (*Caution:* because of the liberation of 2 equiv of carbon dioxide, there is considerable internal pressure which is released; suitable safety protection should be taken). The contents were diluted with water (30 ml) and extracted with chloroform (10 × 15 ml). The combined organic layers were dried and evaporated to leave **8a** as a gum which slowly crystallized (1.81 g, 95%). Recrystallization from ether–dichloromethane afforded white crystals: mp 157.5–158°; 7.35 (s, 1, -COOH), 5.63 (br d, J = 5.5 Hz, 1), 5.42 (br d, J = 5.5 Hz, 1), 4.85–5.2 (br m, 1), 3.1–3.85 (br m, 6, >CHCO- and methines), and 1.8–2.65 (semiperturbed AB, 2, methylenes).

Anal. ($C_{12}H_{12}O_4$) C, H.

B. In an Open Vessel. A slurry of **7** (7.90 g, 33.9 mmol) in concentrated aqueous hydrochloric acid (120 ml) was vigorously stirred and heated to ca. 60° at which point the mixture was maintained for 30 min. The temperature was then increased to maintain reflux for 28 hr. The cooled reaction mixture was poured onto cracked ice (500 g) and extracted with chloroform (10 × 200 ml). Work-up as above provided 6.1 g (82%) of a residue which crystallized. ^{1}H NMR analysis showed the desired acid lactone **8a** to be the nearly exclusive product.

Esterification of 8a. A 900-mg sample of **8a** dissolved in ether (25 ml) was treated with ethereal diazomethane until a faint yellow color persisted. Solvents were removed in vacuo to leave an oil (903 mg). An analytical sample of **8b** was prepared by VPC purification: ν_{max} (neat) 1767 and 1732 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 5.82 (br d, J = 5.5 Hz, 1), 5.56 (br d, J = 5.5 Hz, 1), 4.64–4.86 (br m, 1),

3.68 (s, 3), 3.0-3.75 (br m, 6), and 1.8-2.39 (perturbed AB, 2).

Anal. ($C_{13}H_{14}O_4$) C, H.

Iododecarboxylation of 8a. Acid lactone **8a** (500 mg, 2.4 mmol) was dissolved in refluxing carbon tetrachloride (50 ml), and lead tetraacetate (1.06 g, 2.4 mmol, dried over P_2O_5 and KOH) was introduced under an atmosphere of nitrogen. The stirred suspension was irradiated with a 250-W tungsten lamp (alternatively a 250-W G.E. unfiltered infrared lamp was used) for 20 min, and then iodine (400 mg) in carbon tetrachloride (5 ml) was added dropwise until the mixture remained a permanent pink color. The cooled reaction mixture was filtered and washed with saturated sodium thiosulfate (25 ml) and sodium bicarbonate solutions (2 × 15 ml). Evaporation of the dried solution gave 410 mg (56%) of 9 as white crystals, mp 153-154° (from methanol); ν_{max} ($CHCl_3$) 1770 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 5.55-5.84 (m, 1), 5.3-5.54 (m, 1), 4.8-5.1 (m, 1), 4.76 (s, 1), 3.2-4.0 (m, 4), and 1.95-2.7 (m, 2).

Anal. ($C_{11}H_{11}IO_2$) C, H, I.

Hydrolysis-Dehydroiodination of 9. Iodolactone **9** (740 mg, 2.45 mmol) was stirred together with potassium carbonate (740 mg) in tetrahydrofuran (35 ml) and water (35 ml) for 4 days at room temperature. Solvent was partially removed under reduced pressure, and to the remainder was added water (10 ml) so as to form a colorless solution. This aqueous phase was washed with dichloromethane (3 × 15 ml), then carefully acidified by the dropwise addition of concentrated hydrochloric acid. The mixture was extracted with dichloromethane (3 × 20 ml), dried, and evaporated under reduced pressure to afford white crystals (from ether) of the hydroxy acid: mp 152-153° (321 mg, 68.5%); ν_{max} ($CHCl_3$) 3500-2500 and 1680 cm^{-1}; δ_{Me_4Si} ($CDCl_3$/Me_2SO-d_6) 7.7 (br s, 1), 6.75 (br d, 1), 5.5-5.9 (m, 2), 4.1-4.6 (m, 1), 3.5-3.9 (m, 1), 2.6-3.5 (m, 4), and 1.2-2.4 (m, 2).

Anal. ($C_{11}H_{12}O_3$) C, H.

A solution of this hydroxy acid (130 mg) in ether (15 ml) was treated with a slight excess of diazomethane. Removal of the solvent left hydroxy ester **10** as a colorless oil (138 mg, 99%); ν_{max} (neat) 3500 and 1720 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 6.86 (br d, J = 2 Hz, 1), 5.6-5.95 (m, 2), 4.2-4.6 (m, 2), 3.75 (s, 3), 2.75-3.75 (m, 4), and 1.4-2.4 (m, 2); *m/e* (calcd for $C_{12}H_{14}O_3$, 206.0943) 206.0945.

Mesylation of 10. A solution of **10** (3.4 g, 16.5 mmol) in pyridine (18 ml) was added dropwise to a solution of methanesulfonyl chloride (1.83 ml, 2.69 g, 12.6 mmol) in pyridine (9 ml) at 0° under nitrogen. After stirring for 5 hr, the reaction mixture was poured into 10% aqueous hydrochloric acid (150 ml) and extracted with ether (3 × 200 ml). The combined organic layers were washed with saturated aqueous sodium chloride solution and dried. Evaporation and recrystallization from ether provided 3.61 g (77%) of **11** as a white solid: mp 105-106°; δ_{Me_4Si} ($CDCl_3$) 6.9 (br d, 1), 5.6 (br s, 2), 5.2 (apparent q, 1), 3.4-4.0 (m, 4), 3.73 (s, 3), 2.85 (s, 3), and 2.2 (apparent t, 2).

Anal. ($C_{13}H_{16}O_5S$) C, H.

Methyl Triquinacene-2-carboxylate (12a). A. Dehydration of 10. A solution of **10** (350 mg, 1.7 mmol) in dry tetrahydrofuran (4 ml) was added dropwise to a solution of ethyl(carboxysulfamoyl)triethylammonium hydroxide inner salt[13] (533 mg, 2.4 mmol) in tetrahydrofuran (2 ml) under a nitrogen atmosphere. The mixture was stirred at room temperature for 1 hr at which time the solvent was evaporated to leave a yellow oil. Ether (60 ml) and 10% hydrochloric acid (25 ml) were added and, after shaking, the organic phase was separated, washed with brine (20 ml), and dried. Removal of solvent and molecular distillation furnished pure **12a** as a colorless liquid (178 mg, 56%); ν_{max} (CCl_4) 1720 cm^{-1}; δ_{TMS} ($CDCl_3$) 6.64 (br s, 1), 5.5-5.95 (m, 4), 3.7-4.1 (m, 4), and 3.73 (s, 3); *m/e* (Calcd for, $C_{12}H_{12}O_2$, 188.0837) 188.0840.

Anal. ($C_{12}H_{12}O_2$) C, H.

B. Elimination of 11. A solution of **11** (2.84 g, 10 mmol) in dichloromethane (60 ml) was treated with 51 g of neutral aluminum oxide (activity I). The mixture was stirred vigorously at room temperature for 12 hr, whereupon the alumina was separated by filtration and washed well with dichloromethane. Evaporation of the combined filtrates left 1.38 g (74%) of **12a**, the spectra of which were identical with those recorded for the previous sample.

Triquinacene-2-carboxylic Acid (12b). A solution of **12a** (1.68 g, 8.95 mmol) in ethanol (85 ml) and water (30 ml) was treated with a solution of potassium hydroxide (1.68 g) in water (25 ml). This reaction mixture was heated at 70° for 2 hr, cooled, poured into water (400 ml), and extracted with ether (250 ml). Acidification with 10% hydrochloric acid, followed by ether extraction (3 × 250 ml), drying, and evaporation, yielded 1.55 g (100%) of **12b**: mp 131-133° (from ether-hexane); ν_{max} (CCl_4) 1690, 1425, 1285, and 1272 cm^{-1}; λ_{max} (C_2H_5OH) 224 nm (ε 6230).

Anal. ($C_{11}H_{10}O_2$) C, H.

Resolution of 12b. A solution of **12b** (1.34 g) in methanol (9.5 ml) and water (2.5 ml) was treated with *d*-(+)-α-phenethylamine (0.93 g). After several hours at room temperature, the mixture was allowed to stand overnight in a refrigerator. The first crop of crystals was subjected to repeated recrystallization from methanol-water until the optical rotation at 365 nm showed no further change ($[\alpha]_{365}$ −97.8° (*c* 0.2, ethanol)). Usually three to four recrystallizations sufficed. By this procedure, 347 mg of thick needles was obtained.

Treatment of 235 mg of this (−)-salt with 5% aqueous hydrochloric acid (5 ml) followed by ether extraction (5 × 15 ml), drying, and evaporation provided 130 mg (95%) of optically pure (−)-**12b**; $[\alpha]_D$ −12.4°; $[\alpha]_{365}$ −336° (*c* 0.5, ethanol). After recrystallization from ether-hexane, the white crystals melted at 131-132°; $[\alpha]_D$ −12.3°; $[\alpha]_{365}$ −336° (*c* 0.5, ethanol). The infrared spectrum was identical with that of racemic **12b**.

Preparation of Amide 13. To a sample of acid **12b** (30.7 mg, 0.172 mmol, $[\alpha]_{365}$ +13.0°) in dry benzene (2.1 ml) was added a solution of oxalyl chloride (0.29 ml, ca. 430 mg, 3.4 mmol) in benzene (0.75 ml) at 0°, and the resulting mixture was stirred for 45 min at 0°. Low-boiling materials were removed under reduced pressure. To the crude acid chloride in benzene (2 ml) was added 40 μl of pyridine and 45 μl of *d*-(+)-α-phenethylamine (ca. twofold excess). The resulting mixture was stirred at room temperature for 30 min, added to water (10 ml), and extracted with ether (40 ml). After washing with 10% aqueous hydrochloric acid (10 ml) and water (10 ml), drying, and evaporation, there was obtained 46 mg of crude residue whose ^1H NMR spectrum ($CDCl_3$) featured doublets (J = 7 Hz) at δ 1.47 and 1.45; δ_{Me_4Si} (C_6D_6) 6.9-7.3 (m, 5), 5.0-6.2 (m, 7), 3.8-4.2 and 3.0-3.6 (m, 4), 1.29 and 1.24 (d, J = 6.6 Hz). The ratio of diastereomers (peak height measurements) was ca. 55/45; *m/e* (calcd for $C_{19}H_{19}NO$, 277.1466) 277.1471.

Application of the above reaction sequence to a 25-mg (0.14 mmol) sample of chiral **12b** ($[\alpha]_D$ −12.4°; $[\alpha]_{365}$ −336° (*c* 0.5, ethanol)) led to isolation of 33 mg (86%) of **13**, ^1H NMR analysis (C_6D_6) of the crude product revealed a single diastereomer to be present whose methyl group signal appeared at δ 1.24. The diastereomeric purity of this sample was ≥95%, assuring that the enantiomeric purity of acid (−)-**12b** was also ≥95%.

Anal. ($C_{19}H_{19}NO$) C, H, N.

Preparation of Amide 15. A solution of enantiomerically homogeneous (−)-**12b** (25 mg, 0.14 mmol) in benzene (2 ml) was treated with oxalyl chloride (430 mg, 3.4 mmol) in benzene (0.8 ml) at 0°. After stirring for 45 min at this temperature, solvent and excess oxalyl chloride were removed under reduced pressure. The resulting acid chloride was dissolved in benzene (1 ml) and treated with a solution of bornanamine[46] (**14**, 54 mg, 0.35 mmol) and pyridine (40 μl) in benzene (0.5 ml). This mixture was stirred at room temperature for 1 hr, added to 15 ml of 10% hydrochloric acid, and extracted with 50 ml of ether. The organic layer was washed with water (10 ml), dried, and evaporated to give 50 mg of white crystalline solid. The product was purified by preparative TLC (80-20 ether-carbon tetrachloride) on silica gel to give material which was recrystallized from ethanol-water: mp ca. 175° dec; $[\alpha]^{18}_D$ −40.4°; $[\alpha]^{18}_{365}$ −400° (*c* 0.4, methanol).

Anal. ($C_{21}H_{27}NO$) C, H, N.

(±)-2,3-Dihydrotriquinacen-2-one (16). A solution of racemic **12b** (85.4 mg, 0.49 mmol) in *tert*-butyl alcohol (3.0 ml, redistilled) was treated with diphenylphosphonic azide (158 mg, 0.575 mmol) and triethylamine (75 μl, 0.54 mmol). The resulting solution was heated at 60° for 4.5 hr, cooled to room temperature, and treated with water (3 ml) and 2 *M* hydrochloric acid (10 drops). After being stirred for 1 hr, the mixture was diluted with ether (40 ml) and washed with 1.0 *N* sodium hydroxide solution (5 ml) and water (10 ml). The ether layer was dried and evaporated. Rapid Kugelrohr distillation [95-110° (20 mm)] followed by preparative VPC (6 ft × 0.25 in. 5% SE-30 on Chromosorb G, 115°) provided 32.6 mg (46%) of (±)-**16** as a colorless oil: ν_{max} (CCl_4) 3060, 2970, 2900, 1740, 1410, 1350, 1160, and 910 cm^{-1}; λ_{max} (C_2H_5OH) 297 nm (ε 88); δ_{Me_4Si} ($CDCl_3$) 5.86 (m, 2, olefinic),

5.54 (m, 2, olefinic), 3.8-4.2 (m, 1, methine), 3.2-3.8 (m, 3, methines), 2.3-2.7 (m, 2, $-CH_2CO-$).

(+)-2,3-Dihydrotriquinacen-2-one (16). A solution of **(−)-12b** (104 mg, 0.595 mmol) was treated with diphenylphosphonic azide and triethylamine as described for the racemic acid. Preparative VPC isolation provided 40 mg of colorless oil whose spectral features were identical with those of the racemic ketone. A further purification was undertaken prior to the optical measurements: $[\alpha]^{25}D$ +450°; $[\alpha]^{25}_{578}$ +474°; $[\alpha]^{25}_{546}$ +558°, $[\alpha]^{25}_{436}$ +1192°; $[\alpha]^{25}_{365}$ +2864° (*c* 0.51, ethanol).

Silyl Ether 18. To a solution of **17**[15,26] (5.66 g, 34.5 mmol) in dry dimethylformamide (20 ml) were added *tert*-butyldimethylchlorosilane (6.23 g, 41.5 mmol) and imidazole (5.86 g, 86.4 mmol) in rapid succession. The resulting solution was stirred at room temperature under nitrogen for 18 hr, added to water (200 ml), and extracted with ether (3 × 175 ml). The combined organic layers were dried and concentrated to provide a residue which was filtered through a very short silica gel column (ether-pentane elution). Kugelrohr distillation furnished 9.27 g (96%) of **18** as a colorless oil: bp 115° (0.05 mm); ν_{max} (CCl_4) 1745 cm^{-1}; δ_{Me_4Si} (C_6D_6) 5.05-5.50 (m, 2, olefinic), 4.17-4.53 (m, 1, >CH—O-), 1.50-3.28 (m, 8, methines and methylenes), 0.95 (s, 9, $(CH_3)_3C-$), 0.13 and 0.07 (s, 3 each, $-CH_3$); mass spectrum (70 eV) shows a daughter ion at *m/e* 221 resulting from loss of *tert*-butyl from the parent ion (278 − 57).

Enol Phosphate 20a. To a solution of *n*-butyllithium (0.91 ml, 2.0 mmol) in tetrahydrofuran (4 ml) at −78° was added diisopropylamine (200 mg, 2.0 mmol). A solution of **18** (555 mg, 2.0 mmol) in tetrahydrofuran (4 ml) was added dropwise. After several minutes of stirring, the mixture was treated with diethylphosphorochloridate (345 mg, 2.0 mmol) and tetramethylethylenediamine (2.0 ml), allowed to warm to room temperature with stirring for 2 hr, and quenched by the addition of saturated ammonium chloride solution. The reaction mixture was added to water (40 ml) and extracted with dichloromethane (3 × 75 ml). The combined organic layers were dried and concentrated to give a residue which was taken up in ether and passed through a short silica gel column (ether elution). Evaporation of solvent gave 760 mg (92%) of **20a** which could be conveniently distilled (Kugelrohr) at 165° (0.05 mm) as a colorless oil: δ_{Me_4Si} ($CDCl_3$) 5.44-5.80 (m, 2, olefinic), 5.19-5.34 (m, 1, olefinic), 4.33-4.58 (m, 1, >CH—O-), 3.87-4.33 (m, 4, $-OCH_2-$), 2.78-3.64 (m, 4, methines), 1.3-2.04 (m, 2, methylene), 1.28 (apparent t, 6, $-CH_2CH_3$), 0.82 (s, 9, $-C(CH_3)_3$), and 0.0 (s, 6, $-SiCH_3$).

Bis(*N,N*-dimethylamino)phosphate (20b). To a solution of lithium diisopropylamide prepared from *n*-butyllithium in hexane (6.75 mmol) and diisopropylamine (0.95 ml, 6.75 mmol) in tetrahydrofuran (10 ml) at −78° were added 1.70 g (6.10 mmol) of **18,** 5.20 g (30.5 mmol) of bis(*N,N*-dimethylamino)phosphorochloridate, and tetramethylethylenediamine (5.0 ml) dissolved in tetrahydrofuran (10 ml). After being stirred at room temperature for 4 hr, the reaction mixture was processed as above to give 1.29 g (52%) of **20b**: δ_{Me_4Si} (C_6D_6) 5.28-5.77 (m, 3, olefinic), 4.60-4.78 (m, 1, >CHO-), 2.84-3.60 (m, 4, methines), 2.44 (d, $^3J_{PH}$ = 11 Hz, 12, >N—CH_3), 1.17-2.08 (m, 2, methylene), 0.93 (s, 9, $-C(CH_3)_3$), 0.08 and 0.07 (s, 6, $-SiCH_3$, $\Delta\nu \sim 1$ Hz); *m/e* (calcd for $C_{16}H_{28}N_2O_3PSi$, 355.1607) 355.1611.

exo-2,3-Dihydro-2-(*tert*-butyldimethylsilyloxy)triquinacene (21). To a solution of lithium (1.13 g, 162 mg-atoms) in ammonia (270 ml) at −78° under argon was added at solution of **20a** (13.54 g, 32.8 mmol) and *tert*-butyl alcohol (2.95 ml, 35.7 mmol) in tetrahydrofuran (95 ml). The reaction mixture was stirred at −78° for 1.5 hr, quenched by the cautious addition of water, and kept at room temperature to permit evaporation of ammonia. Further dilution with water was followed by ether extraction and subsequent processing of the combined ether phases. Kugelrohr distillation of the residue [80-85°/(0.05 mm)] furnished 6.86 g (80%) of **21** as a colorless oil: δ_{Me_4Si} (C_6D_6) 5.20-5.67 (m, 4, olefinic), 4.06-4.29 (m, 1, >C*H*—O-), 2.87-3.66 (m, 4, methines), 1.42-2.00 (m, 2, methylene), 0.92 (s, 9, $-C(CH_3)_3$), and 0.03 (s, 6, $-SiCH_3$).

Anal. ($C_{16}H_{26}OSi$) C, H.

To a solution of lithium (19 mg, 2.7 mg-atoms) in ammonia (4 ml) at −78° under argon was added via syringe a solution of **20b** (210 mg, 0.545 mmol) and *tert*-butyl alcohol in tetrahydrofuran (2 ml). The mixture was stirred at −78° for 1.5 hr and quenched by the addition of water. After pouring into water (15 ml), the product was extracted with ether (2 × 15 ml), and the organic layers were dried and concentrated. There was obtained 130 mg (92%) of a colorless oil, the ^1H NMR spectrum and VPC behavior of which showed it to be identical with the sample of **21** prepared above.

exo-2,3-Dihydrotriquinacen-2-ol (22). A solution of **21** (6.86 g, 27.5 mmol) in tetrahydrofuran (50 ml) was added to a cooled solution of tetrabutylammonium fluoride[27] (17.5 g, 64 mmol) in tetrahydrofuran (100 ml). The mixture was stirred at room temperature for 2.5 hr, added to 600 ml of water, and extracted with ether (2 × 400 ml). The aqueous layer was saturated with sodium chloride and again extracted with ether. The combined organic layers were dried and concentrated to give a residue which was chromatographed on silica gel eluting with pentane and then with 30% ether in pentane. In this manner, 3.70 g (90%) of pure **22**[25] was obtained.

exo-2,3-Dihydrotriquinacen-2-ol Phthalate (23). A mixture of **22** (203 mg, 1.38 mmol), sublimed phthalic anhydride (205 mg, 1.38 mmol), and pyridine (3 ml) was heated in an oil bath at 90-95° for 4 hr. The cooled reaction mixture was added to 2 *M* hydrochloric acid and extracted with dichloromethane (3 × 50 ml), and the combined layers were processed in the usual manner to give 380 mg (93%) of very viscous residue which failed to crystallize: ν_{max} (CCl_4) 1700, 1410, 1290, and 1125 cm^{-1} in addition to a very broad absorption band in the 2850-3100 region; δ_{Me_4Si} ($CDCl_3$) 9.78 (br s, -OH), 7.34-8.00 (m, 4, aromatic), 5.23-6.00 (m, 5, olefinic and >C*H*—O-), 2.92-3.87 (m, 4, methines), and 1.38-2.43 (m, methylene).

Attempts to efficiently resolve **23** with such bases as *l*-cinchonidine, brucine, (+)-α-phenethylamine, and dehydroabietylamine proved unsuccessful.

Oxidation of 22.[47] A dichloromethane solution of chromium trioxide-dipyridine complex [from 4.05 g (40.5 mmol) of CrO_3 and 6.30 g (81.0 mmol) of dry pyridine in 100 ml] was treated dropwise with a solution of **22** (1.0 g, 6.8 mmol) in dichloromethane. The mixture was stirred for 30 min at room temperature, and the liquid phase was decanted from insoluble solid formed during the reaction. The gummy solid was triturated with ether (2 × 25 ml), and the combined organic layers were evaporated. The residue was taken up in ether and washed with 5% hydrochloric acid, sodium bicarbonate solution, and brine before drying and concentration. There was obtained 840 mg (85%) of racemic **16.**

2,3-Dihydrotriquinacen-2-one Carboxymethoxime (24a). A solution of racemic **16** (1.40 g, 9.60 mmol) and (aminooxy)acetic acid hydrochloride (1.10 g, 5.04 mmol) in ethanol (7 ml) and water (0.5 ml) was treated with sodium acetate (690 mg, 5.04 mmol) dissolved in a minimal amount of water. The mixture was heated to reflux for 30 min and allowed to stand at room temperature for 2 days. Most of the ethanol was removed under reduced pressure to give a residue which was treated with chloroform and saturated brine. The aqueous layer was twice extracted with chloroform, and the combined organic layers were washed with saturated brine. Drying and solvent removal left 2.1 g (100%) of white crystalline **24a**: mp 98-104°; δ_{Me_4Si} ($CDCl_3$) 10.6 (s, 1, -OH), 5.37-6.00 (m, 4, olefinic), 4.60 (s, 2, $-CH_2O-$), and 2.04-4.36 (br m, 6, methines and methylene).

Attempts to resolve this material with dehydroabietylamine and (+)-α-phenethylamine failed to produce **16** (after acid hydrolysis) having greater than 37% enantiomeric purity.

(+)-Tricyclo[5.2.1.0^{4,10}]decan-2-one (25). A sample of enantiomerically pure (+)-**16** (20 mg) dissolved in ethyl acetate (5 ml) was treated with 10% Pd/C (15 mg), and the mixture was shaken under 40 psig of hydrogen in a Parr apparatus for 1 hr. VPC analysis (10 ft × 0.125 in. 15% Carbowax 20M on Chromosorb P, 160°) of the residue obtained after filtration and concentration of the filtrate showed one component and no trace of **16.** The product was purified on a 6-ft 5% SE-30 column (125° to give (+)-**25** as a white solid: mp 72-75°; $[\alpha]^{27}_{365}$ +305°; $[\alpha]^{27}_{436}$ +136°; $[\alpha]^{27}_{546}$ +67°; $[\alpha]^{27}_{578}$ +58° (*c* 0.08, ethanol). The ir and ^1H NMR spectra of this ketone were identical with those of the previously reported racemic compound.[36]

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