A correction for secondary extinction was applied according to the equation[12]

$$(F_c^*)^2 = \frac{F_c^2}{1 + g\beta F_c^2}$$

The parameter, g, was refined in the least squares. With the hydrogen atoms and secondary extinction factor included, the refinement was continued until shifts in all positional and thermal parameters were less than $^1/_3$ standard deviations. The final R for these refinements was 0.076. The

$$\text{weighted } R = \left\{\frac{\Sigma\omega(|F_o|^2 - |F_c|^2)^2}{\Sigma\omega|F_o|^4}\right\}^{1/2} = 0.13$$

and the standard deviation of fit =

$$\left\{\frac{\Sigma\omega(|F_o|^2 - |F_c|^2)^2}{m - s}\right\}^{1/2} = 1.90$$

(12) A. C. Larson, *Acta Crystallogr.*, **23**, 664 (1967).

The standard deviation of fit is expected to be 1.0 if the refinement has converged and if the weighting scheme and structural model are adequate.

The final parameters are listed in Table I. The final value of the secondary extinction parameter, g, is 1.041×10^{-5}. A table of observed and calculated structure factors has been deposited with the National Auxiliary Publication Service.[13] All calculations were done on the IBM 360 computer using programs of the CRYM system written by one of the authors (D. J. Duchamp).

Registry No.—IV, 31128-90-2.

(13) Listings of structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

Conformation and Reactivity in the *cis,trans*-2,6-Cyclodecadienyl System[1,2]

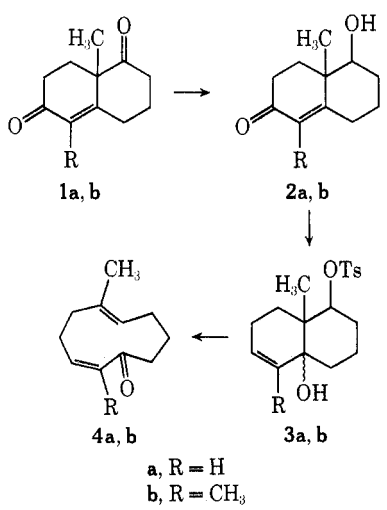
P. S. WHARTON* AND M. D. BAIRD

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

Received February 23, 1971

6-Methyl- and 2,6-dimethyl-*cis,trans*-2,6-cyclodecadienones (**4a** and **4b**) were synthesized by fragmentation of octalin diol monotosylates. They exhibit the properties of twisted α,β-unsaturated ketones. 2,6-Dimethyl-*cis,trans*-2,6-cyclodecadienyl methyl ether exists in two conformations in carbon disulfide (70:30 at −62°). Solvolysis of the corresponding *p*-nitrobenzoate (**5** PNB) in buffered acetic acid at 30° yielded exclusively *trans*-bicyclo[5.3.0] products, and it is tentatively concluded that participation of the C-6,7 double bond contributes significantly to the solvolytic rate.

Ten-membered rings have been of unusual interest with respect to the stereochemisty of transannular reactions.[3] The following study of the *cis,trans*-2,6-cyclodecadienyl system, originally undertaken with thoughts of sesquiterpene synthesis, is exemplary.



6-Methyl-*cis,trans*-2,6-cyclodecadienone (**4a**) was prepared by fragmenting hydroxy tosylate **3a** with potassium *tert*-butoxide in *tert*-butyl alcohol.[4] Cyclodecadienone **4a** was obtained in 20% overall yield from ketol **2a**[5] by conversion of the ketol to a crystalline tosylate which was then subjected to epoxidation, hydrazine reduction, and fragmentation, without isolation of intermediates.[6] Dienone **4a**, obtained by this method, exhibits the properties of a twisted α,β-unsaturated ketone. The ultraviolet maximum at 228 nm in ethanol is of low intensity, ϵ 4680.[7] The relative nmr shifts of the α and β hydrogens are reversed from normal, with the β hydrogen at τ 4.4 at higher field than the α hydrogen at τ 3.8.[7] The stereochemistry of the double bonds of **4a** must be cis-2 (unchanged during the reaction, with the vinyl hydrogens showing a coupling constant of 11.5 Hz[7]) and trans-6 (determined by the geometrical constraint of the fragmentation step[8]).

2,6-Dimethyl-*cis,trans*-2,6-cyclodecadienone (**4b**) was then synthesized, without further study of **4a**. It was prepared in 64% overall yield by the procedure already described but starting from ketol **2b**.[9] The new dienone differs from **4a** solely by the presence of a methyl group at C-2, but this additional methyl group greatly facilitated analysis of a reaction described later

(1) This investigation was supported by Public Health Service Research Grants GM 14133 and GM 16338 from the Division of General Medical Sciences, U. S. Public Health Service.

(2) This article is abstracted from the Ph.D. thesis of M. D. B., University of Wisconsin, 1969. The research was carried out in part at Wesleyan University.

(3) For a survey of transannular reactions in medium-sized rings see A. C. Cope, M. M. Martin, and M. A. McKervey, *Quart. Rev., Chem. Soc.*, **20**, 119 (1966).

(4) Under similar conditions formation of another 2,6-cyclodecadienone by fragmentation–elimination has been demonstrated by M. Iguchi and A. Nishiyama, *Tetrahedron Lett.*, 4295 (1969).

(5) C. B. C. Boyce and J. S. Whitehurst, *J. Chem. Soc.*, 2680 (1960).

(6) This sequence is superior to that originally used to prepare 6-methyl-*trans*-5-cyclodecenone, which unnecessarily involved benzoylation of ketol **2a** and subsequent saponification; see P. S. Wharton, *J. Org. Chem.*, **26**, 4781 (1961).

(7) *cis*-2-Cyclodecenone exhibits a uv maximum at 227 nm in ethanol with ϵ 3500 and nmr chemical shifts for the α and β protons at τ 3.67 and 4.23, respectively, $J_{2,3}$ = 11.9 Hz. For further comparison the following constants are also noted: *cis*- and *trans*-2-cycloundecenones, $J_{2,3}$ = 12.1 and 16.7 Hz, respectively; *cis*- and *trans*-2-cyclododecenones, $J_{2,3}$ = 11.6 and 15.9 Hz, respectively. See M. Regitz and J. Ruter, *Chem. Ber.*, **102**, 3877 (1969).

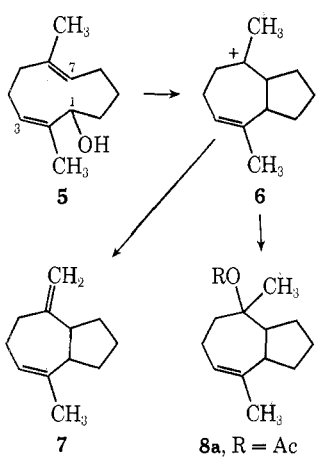
(8) P. S. Wharton and G. A. Hiegel, *J. Org. Chem.*, **30**, 3254 (1965), and references cited therein.

(9) V. F. Kucherov and I. A. Gurvich, *Zh. Obshch. Chim.*, **31**, 796 (1961); *J. Gen. Chem. USSR*, **31**, 731 (1961).

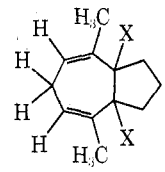
The spectroscopic properties of dienone **4b** were similar to those of **4a**: a low-intensity (ϵ 4200) ultraviolet maximum at 239 nm in ethanol and a high-field chemical shift of τ 4.6 for the β proton of the α,β-unsaturated ketone.

2,6-Dimethyl-*cis,trans*-2,6-cyclodecadienol (5), a solid, mp 79°, was obtained by reduction of the corresponding dienone with lithium aluminum hydride. Certain deuterium-labeled compounds were similarly prepared. Reduction with lithium aluminum deuteride yielded **5**-1-d_1. In addition, by reducing dione **1b** initially with sodium borodeuteride, it was possible to prepare **5**-7-d_1 and **5**-1,7-d_2. Labeling with deuterium established the unrearranged location of the hydroxyl group and enabled straightforward nmr assignments to be made to the three hydrogens at τ 5.84 (C-1), 5.16 (C-7), and 4.84 (C-3).

Dienol **5** was found to be unstable at 150°, affording products apparently derived from cyclization. The corresponding methyl ether and acetate behaved similarly and the acetate also yielded similar products upon solvolysis in buffered acetic acid at room temperature. It was, however, cyclization of the corresponding *p*-nitrobenzoate (**5** PNB), mp 80°, a nicely crystalline derivative, which was most conveniently studied.[10] Solvolysis in buffered acetic acid at room temperature gave a mixture which was separated by a combination of crystallization and thick layer chromatography into olefin (46%), acetate (46%), and PNB (8%) fractions. According to the criteria of glpc, tlc, and various spectroscopic data, each fraction consisted essentially of one component (but the presence in each fraction of small amounts of compounds with similar properties is not excluded). Spectroscopic data characterized the olefin, acetate, and PNB as **7**, **8a**, and **8b**, respectively. Thus

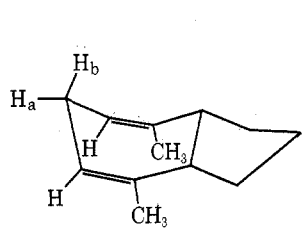


all the products were produced, in a formal sense, by Markovnikov addition of the C-1 carbon of the incipient allyl cation to the C-6,7 double bond, generating ion **6**.[11] The three products were readily shown to have the same stereochemistry of ring fusion: acetate and PNB were interconverted by reduction–esterification and, upon pyrolysis, acetate yielded olefin in 47% yield. The pyrolysis also afforded, in 53% yield, another olefin (**9a**) which made possible the assignment of stereochemistry to the ring fusion. This was accomplished by inspec-

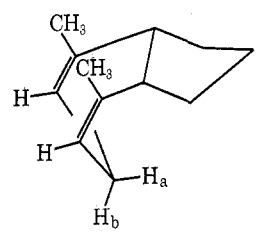


9a, X = H
b, X = D

tion of the nmr spectrum of **9b**, obtained from acetate derived from solvolysis of the PNB of **5**-1,7-d_2. The two doubly allylic methylene protons appeared as a pattern consisting of a triplet of septuplets with J = 5.8 Hz for the coupling with the two vinyl hydrogens and J = 1.3 Hz for the coupling with the six methyl protons. The spectrum of this region was broadened but not grossly changed down to −84°. This pattern is consistent with the equivalence of the methylene protons in a molecule with a trans ring fusion but cannot be explained for the nonequivalent methylene protons of cis-fused diene. In *trans*-diene a very facile wagging motion of the methylene group of the 1,3-cycloheptadiene ring interconverts identical conformations and makes the two protons equivalent. Some extraordinary coincidences would have to occur for the observed pattern to arise from *cis*-diene, and such a possibility can be dismissed as follows. *cis*-Diene can exist in two



10



11

conformations, **10** and **11**, also interconvertible by a wagging motion of the methylene group. They are not identical. If *cis*-diene should exist solely in conformation **10** the two methylene protons might have coincidental chemical shifts but they would not be coupled equally to the vinyl[12] or methyl[13] hydrogens (dihedral angles 10 and 130° from models). If *cis*-diene should exist as equal amounts of the two conformations the couplings would be averaged but the two protons could not absorb at the same chemical shift: in conformation **11** H_a lies directly under the cyclopentane ring and should be shielded, relative to H_b in either conformation or H_a in conformation **10**, by *ca.* 24 Hz (at 60 MHz).[14] The averaged shift difference of 12 Hz is more than enough to exclude the possibility in the coupling pattern of a set of simple septuplets with J = 1.3 Hz.

Inspection of Dreiding models reveals no immediately obvious reason why products with a cis ring fusion

(10) A similar cyclization has been reported by J. A. Marshall and W. F. Huffman, *J. Amer. Chem. Soc.*, **92**, 6358 (1970).

(11) Formation of a carbon–carbon bond involving the C-3 carbon of the incipient allylic cation seemed unlikely from inspection of Dreiding models and it was straighforward to show that this mode of cyclization was inconsequential. Solvolysis of **5**-1-d_1 PNB yielded products with nmr absorption corresponding to one vinyl hydrogen at C-3. Dehydrogenation of the total product yielded 4,8-dimethylazulene (one singlet at τ 7.15) with no trace of 1,4-dimethylazulene [two singlets at τ 7.38 and 7.22 reported by D. Mueche and S. Huneck, *Chem. Ber.*, **99**, 2669 (1966)].

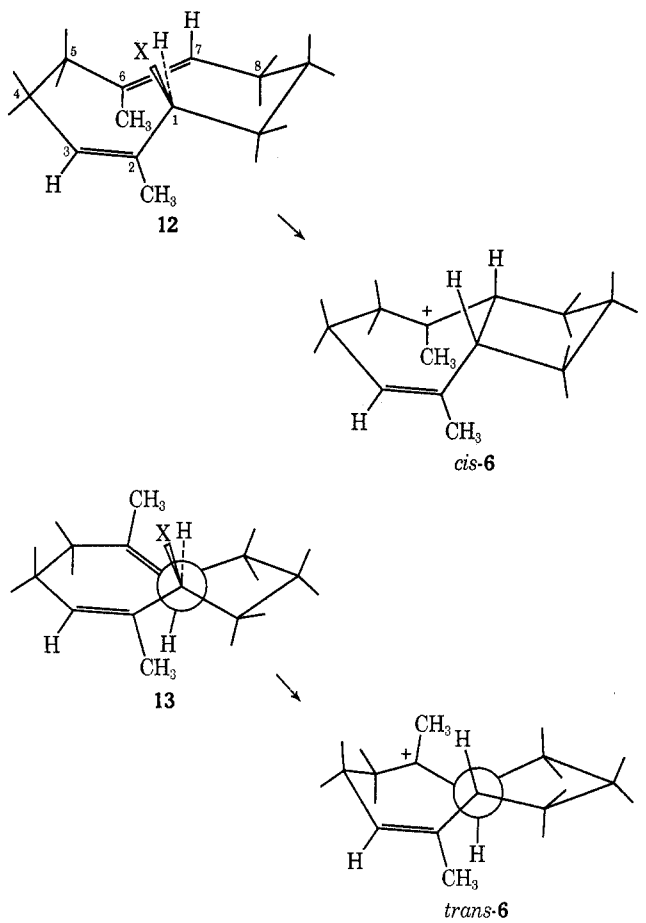
(12) K. L. Williamson and W. S. Johnson, *J. Amer. Chem. Soc.*, **83**, 4623 (1961).

(13) J. T. Pinkey and S. Sternhell, *Tetrahedron Lett.*, 275 (1963).

(14) The calculation employed $\chi_L - \chi_T = 5.5 \times 10^{-30}$ ml molecule^{-1}, and the McConnell equation; see A. A. Bothner-By and C. Naar-Colin, *Ann. N. Y. Acad. Sci.*, **70**, 833 (1958), and H. M. McConnell, *J. Chem. Phys.*, **27**, 226 (1957).

should not form from a process involving simple allylic ionization. Two conformations (or conformational subsets), **12** and **13**, can readily be defined, interconvertible by rotation of the trans double bond through the ring.[15,16] In each case the two assemblies of carbons containing the double bonds, C-1–4 and C-5–8, define two planes which face each other across the ring. The two conformations can be defined by the relation of the methyl groups as syn (**12**) or anti (**13**) with respect to the overall plane of the ring. The two double bonds are approximately parallel in the syn conformation and crossed in the anti conformation. In each conformation the PNB group, which necessarily lies outside, rather than inside, the ring, is favorably aligned for allylic ionization. The syn conformation is geometrically related to cis product, the anti conformation to trans product.

SCHEME I[a]



[a] Note the unorthodox but hopefully not misleading use of a Newman projection in **13** which serves to separate sets of atoms attached to two *nonbonded* carbon atoms coincident in projection. Compare and contrast with the orthodox use in *trans*-**6**.

Nmr temperature-dependent spectra were revealing with respect to the conformational composition of the ground state of the ten-membered ring. Although neither **5** PNB nor **5** acetate yielded useful data because of insolubility and a coincidence of chemical shifts, respectively, interpretable results were obtained with the methyl ether, using deuterium-established nmr assignments for hydrogens at C-1, -3, and -7. Two conformations were well resolved in the ratio 70:30 at −62° in carbon disulfide. They averaged rapidly on the nmr time scale above −20°. It was possible to correlate the major one with the anti conformation on account of the large shift difference for the C-7 proton in the two conformations, arising from the fact that it lies directly above the C-2,3 double bond in the anti conformation.

It would thus appear that both syn and anti conformations are available to **5** PNB in acetic acid but only trans product is formed, presumably solely from the anti conformation.[17] Participation of the C-6,7 double may well provide the required explanation. A more detailed examination shows that, although the C-1,7 distance in undistorted Dreiding models is less than 3 Å for both conformations, the C-6,7 double bond of the anti conformation can initiate and maintain favorable overlap of the developing transannular bond with less geometric restraint or distortion than can the double bond of the syn conformation; and trans product is almost certainly more stable than cis product.[18]

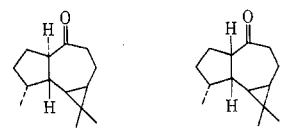
Kinetic data were also suggestive of participation. Solvolysis of **5** PNB in buffered acetic acid at 30° was found to be extremely fast, proceeding with a first-order rate constant of 2×10^{-4} sec^{-1}. This compares with a solvolytic rate constant of 1×10^{-6} sec^{-1} at 100° in 90% aqueous acetone for the similarly substituted PNB of *trans*-α,γ-dimethylallyl alcohol;[19] after allowing for differences of temperature and solvent,[20] **5** PNB is estimated to solvolyze 10^5–10^6 times faster. This is certainly much faster but this fact is unfortunately not immediately interpretable; some relevant comparative rate data are available[21] but until the rate of sol-

(15) This motion in *trans*-cyclodecene, for which E_a = 11 kcal mol^{-1}, has been studied by G. Binsch and J. D. Roberts, *J. Amer. Chem. Soc.*, **87**, 5157 (1965).

(16) Conformational isomerism has been established by nmr for several 1,5-cyclodecadienes: urospermal, R. K. Bentley, J. G. St. C. Buchanan, T. C. Halsall, and V. Thaller, *Chem. Commun.*, 435 (1970); isabelin, H. Yoshioka, T. J. Mabry, and H. E. Miller, *ibid.*, 1679 (1968); neolinderolactone, K. Tori, I. Horibe, K. Kuriyama, and K. Takeda, *ibid.*, 957 (1970); and hedycaryol and 1,5-dimethyl-*trans*,*trans*-1,5-cyclodecadiene, H. C. Kluender and Y. C. Poon, respectively, Ph.D. theses, Wesleyan University, 1971. Individual conformations have been determined by X-ray for germacatriene, F. H. Allen and D. Rogers, *Chem. Commun.*, 588 (1967); pregeigerene J. McClure, G. A. Sims, P. Coggan, and A. T. McPhail, *ibid.*, 128 (1970); and costunolide, F. Sorm, M. Suchy, M. Holub, A. Link, I. Hadinec, and C. Novak, *Tetrahedron Lett.*, 1893 (1970); and by nuclear Overhauser effects for furanodienone and isofuranodienone, H. Hikino, C. Komo, T. Takemoto, K. Tori, M. Ohtsuru, and I. Horibe, *ibid.*, 662 (1969); dihydrotamaulipin A acetate, N. S. Bhacca and N. H. Fischer, *ibid.*, 68 (1969); zeylanine and zeylanane, K. Tori, M. Ohtsuru, I. Horibe, and K. Takeda, *ibid.*, 943 (1968).

(17) Formation of trans product starting from the syn conformation would involve an unlikely combination of steps: allylic ionization, rotation of the trans double bond through the ring, and addition of the allyl cation to the double bond.

(18) See G. Buchi, S. W. Chow, T. Matsuura, T. L. Popper, H. H. Rennhard, and M. Schach V. Wittenau, *Tetrahedron Lett.*, No. 6, 14 (1959). In particular, it was shown that apoaromadendrone (i) is more stable than α-apoaromadendrone (ii).



(19) H. L. Goering and W. D. Closson, *J. Amer. Chem. Soc.*, **83**, 3511 (1961).

(20) The temperature calculation assumed $\Delta H^{\ddagger}$ = 28 kcal mol^{-1} for solvolysis of the PNB of α,γ-dimethylallyl alcohol; see H. L. Goering and E. F. Silversmith, *J. Amer. Chem. Soc.*, **77**, 6249 (1955), and references cited therein. No solvent calculation was necessary because the Y values of acetic acid and 90% aqueous acetone are virtually identical: see A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, p 45.

(21) The relative rates of solvolysis of PNBs of *trans*-5-cyclodecenol, α,γ-dimethylallyl alcohol, and cyclodecanol in 90% aqueous acetone are approximately 10:1:<10^{-2}; see ref 19.

volysis of the PNB of *cis*-2-cyclodecenol has also been determined an estimate of the extent of participation in the solvolysis of **5** PNB is deferred. Participation of this kind is not unknown, occurring, for example, in the solvolytic cyclization of (allylic) esters of linalool and nerol to the terpenyl system.[22]

Experimental Section

Physical Data.—Melting points were determined on a Thomas Unimelt capillary melting point apparatus and are uncorrected. Analyses were performed by Micro-Tech Laboratories, Inc., Skokie, Ill. and Spang Microanalytical Laboratory, Ann Arbor, Mich. Infrared spectra were obtained using Perkin–Elmer Model 137 Infracord and Beckman IR-8 spectrophotometers. Nmr spectra were recorded on Varian Associates A-60 or A-60A instruments employing tetramethylsilane as an internal reference. A Varian V-6040 nmr variable-temperature controller was used for low-temperature work. Ultraviolet spectra were obtained with Cary Models 11 and 15 recording spectrophotometers. Mass spectra were recorded with a Consolidated Electrodynamics Corp. Type 21-203 C mass spectrometer. Gas–liquid phase chromatography (glpc) was performed on Varian Aerograph, Model A-90-P, and Perkin–Elmer Model F-11, units, using packed and capillary stainless steel columns, respectively. The various columns used for glpc were 5 ft × 0.25 in. (1) 5% Carbowax 20M on Teflon-6; (2) 10% Carbowax 20M on Chromosorb P; (3) 20% SF-96 on 60–80 firebrick; and 150 ft × 0.01 in. (4) Ucon 50 HB 2000 Polar; (5) SF-96; (6) Apiezon L.

Materials and Procedures.—All solvents were dried and distilled with the exception of Merck absolute methanol and Mallinckrodt absolute ether. Magnesium sulfate was used as a drying agent. Pyridine was distilled from barium oxide and stored over barium oxide. *p*-Nitrobenzoyl chloride was recrystallized from hexane. Sodium acetate was dried at 110° for 6 hr. Glacial acetic acid was purified by addition of 1% v/v of acetic anhydride and 2% by weight of chromium trioxide and subsequent distillation (bp 115–116°).[23] Preparative tlc was performed on 20 × 20 cm glass plates covered with a 1.5-mm layer of silica gel (Brinkman PF 254).

6-Methyl-2,6-*cis,trans*-cyclodecadienone (4a).—To a slurry of 0.502 g (1.51 mmol) of **2a** tosylate[24] in 16.5 ml of absolute methanol at 0° was added 0.6 ml (21.8 mmol) of 90% hydrogen peroxide and 0.17 ml of 10 *N* aqueous sodium hydroxide solution. After stirring for 2 hr at 0° the reaction mixture was poured into 60 ml of saturated sodium chloride solution. The resulting mixture was extracted with 100 ml of ether. The organic layers were washed with saturated sodium chloride solution and dried. Filtration and evaporation gave 0.528 g (101%) of white solid: mp 104–130°; nmr ($CDCl_3$) τ 9.27–7.6 (complex, 14.4, with equally intense peaks at 8.88 and 8.81) and equally intense singlets at 7.13 and 6.95. To a slurry of 0.500 g (1.44 mmol) of this solid in 10 ml of absolute methanol was added 0.24 ml of glacial acetic acid. The flask was attached to a gas-measuring buret, and 0.24 ml (4.9 mmol) of hydrazine hydrate (99–100%) was added through a septum. The mixture became warm. Gas evolution indicated that the reaction was nearly complete in 3 min; after stirring for 1 hr the total gas evolution was 28.2 ml (64%). The yellow solution was poured into 100 ml of saturated sodium chloride solution and the mixture was extracted with 200 ml of ether. The organic layer was washed with saturated sodium chloride solution, 1.5 *N* sodium hydroxide solution, and saturated sodium chloride solution until neutral and dried. Filtration and evaporation gave 0.412 g which was dissolved in 16 ml of *tert*-butyl alcohol and treated with 3.7 ml of 1 *N* potassium *tert*-butoxide in *tert*-butyl alcohol. The reaction mixture turned cloudy and dark red immediately. After 25 min 10 ml of water was added and the mixture was extracted with 100 ml of hexane. The organic layer was washed with 100 ml of saturated sodium chloride solution and dried. Filtration and evaporation gave 0.183 g of brown oil, short-path distillation of which gave 0.059 g (22% overall) of a colorless oil at a bath temperature of 37–141° (0.1 mm): glpc analysis on column 1 (127°) revealed the presence of only one component; uv max (95% ethanol) 228 nm (ϵ 4860); ir (film) 5.97, 6.20, 10.0, 12.17 13.05, and 13.5 μ; nmr (CCl_4) τ 8.57 (s, 3), 5.27 (t, 1), 4.4 (d of t, 1), 3.79 (d, 1, J = 11.5 Hz). Preparative glpc yielded a sample which was submitted for analysis.

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.23; H, 9.99.

***p*-Toluenesulfonate of 1,4aβ-Dimethyl-4,4a,5,6,7,8-hexahydronaphth-5β-ol-2(3*H*)-one (2b Tosylate).**—To a solution of 99.3 g (0.510 mol) of anhydrous ketol **2b**,[25] bp 150–155° (0.2 mm), in 355 ml of dry pyridine at room temperature was added 198 g (1.04 mol) of tosyl chloride. The reaction mixture was cooled and stirred at 5° for 70 hr. It was then diluted with 2000 ml of water and extracted with four 1000-ml portions of chloroform. The combined chloroform extracts were washed with 2500 ml of 2 *M* hydrochloric acid and 1000 ml of saturated sodium chloride solution and dried. Filtration, evaporation, and crystallization from benzene–hexane gave 146.1 g (82%) of white solid: mp 104–105°: uv max (methanol) 228 nm (ϵ 18,700), 245 (14,500); ir ($CHCl_3$) 6.02 μ; nmr ($CDCl_3$) τ 8.80 (CH_3) and 5.72 (CHOTs). Three recrystallizations from methanol afforded an analytical sample, mp 108–109°.

Anal. Calcd for $C_{19}H_{24}O_4S$: C, 65.50; H, 6.94; S, 9.18. Found: C, 65.44; H, 6.89; S, 9.35.

2,6-Dimethyl-2,6-*cis,trans*-cyclodecadienone (4b).—A slurry of 26.4 g (75.8 mmol) of **2b** tosylate in 551 ml of absolute methanol was warmed to 55°, yielding an amber solution. The solution was then cooled to 30° and 39 ml (1.44 mmol) of 90% hydrogen peroxide was added with stirring. Then 9 ml of 10 *N* sodium hydroxide solution was added dropwise over a 5-min period. A white precipitate formed but did not increase in quantity with time. The reaction mixture was stirred at room temperature for 3 hr[26] and was then poured into 1110 ml of saturated sodium chloride solution, diluted with a further 500 ml of water, and extracted with three 1000-ml portions of ether. The combined organic layers were washed with five 500-ml portions of saturated sodium chloride solution and dried. The final washing gave a negative peroxide test with acidic potassium iodide. Filtration and evaporation gave 27.2 g (99%) of white semisolid epoxide: uv max (methanol) 226 nm; ir ($CHCl_3$) 5.89 μ; nmr ($CDCl_3$) two equally intense methyl peaks at τ 8.94 and 8.82 and 5.44 (CHOTs).

Another run yielded 79.9 g of crude epoxide. This was dissolved in 275 ml of methanol containing 0.8 ml of acetic acid. The flask was attached to a gas meter and 39 ml of hydrazine hydrate was added. Gas evolution reached 4100 ml after 30 min and 5600 ml when the reaction was worked up after 7 hr. The methanol was removed from the reaction mixture on a rotary evaporator and the resulting oil was dissolved in 4000 ml of ether. The ether was washed with water until the washings were neutral. Drying, followed by filtration and evaporation, gave 78.0 g of a yellow oil which was dissolved in 330 ml of *tert*-butyl alcohol and heated with 440 ml of 1 *N* potassium *tert*-butoxide in *tert*-butyl alcohol. A further 250 ml of *tert*-butyl alcohol was added to facilitate stirring, which was continued at room temperature under nitrogen for 30 min. The reaction mixture was then poured into 1500 ml of water. The mixture was extracted with three 1000-ml portions of hexane and the combined organic layers were evaporated at 30°, yielding a brown oil which was dissolved in 1000 ml of hexane, washed with two 500-ml portions of saturated sodium chloride solution, and dried. Filtration and evaporation gave 39.1 g of a brown oil; nmr (CCl_4) showed the presence of *ca.* 5% of a tosylate-containing impurity. Short-path distillation gave 28.4 g of a colorless oil at a bath temperature of 85–107° (0.1 mm). The residue of 8.37 g yielded a further 1.0 g of distillate after trituration with hexane and separation of the hexane solution from insoluble gum. The distillate was identical with material collected from another run: ir (film) 5.96 and 6.15 μ; uv max (hexane) 230 nm (ϵ 5070); uv max (methanol) 239 nm (ϵ 4220); nmr (CCl_4) τ 8.55 and 8.1 (CH_3) and 5.22 and 4.67 (vinyl hydrogens). Glpc on column 1 (125°) showed only one component; on column 4 (125°) 10% of another component was observed which may have been due to decomposition on the column. Preparative glpc on column 1 (125°) furnished an analytical sample.

(22) See W. Rittersdorf and F. Cramer, *Tetrahedron*, **24**, 43 (1968), and references cited therein.

(23) K. J. P. Orton and A. E. Bradfield, *J. Chem. Soc.*, 983 (1927).

(24) C. H. Heathcock, R. A. Badger, and J. W. Patterson, Jr., *J. Amer. Chem. Soc.*, **89**, 4133 (1967).

(25) Crystallization from ether gave white crystals, mp 83–87°, possibly hydrated. The melting point reported by Kucherov (ref 9) is 73–74°.

(26) The reaction was monitored by uv and was worked up when the ratio of absorbances at 288 and 245 nm was 9.5:1.

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 81.08; H, 10.16.

2,6-Dimethyl-2,6-*cis,trans*-cyclodecadienol (5).—To a slurry of 0.184 g (4.86 mmol) of lithium aluminum hydride in 8 ml of ether was added 1.638 g (9.22 mmol) of dienone **4b** in 6 ml of ether over a 20-min period. The reaction mixture was stirred for a total of 60 min at room temperature under nitrogen and then poured into a beaker. Saturated magnesium sulfate solution was added until hydrogen evolution ceased and then anhydrous magnesium sulfate was added until the solid residue was powdery. The slurry was then filtered and the solid was washed with five 100-ml portions of ether. After drying and evaporation the combined filtrate and washings afforded 1.654 g (99%) of white solid, which was sublimed at 40°, giving 1.459 g (88%): mp 73–78°; mass spectrum (70 eV) *m/e* (rel intensity) 180 (0.3), 162 (35), 91 (100); nmr (CCl_4) τ 8.41 and 8.32 (CH_3 doublets with J = 1.3 and 1.45 Hz, respectively), 5.84 (t, 1, J = 7 Hz), 5.16 (t, 1, J = 7 Hz), and 4.88 (t, J = 7 Hz).

Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, C, 79.62; H, 10.93.

Another sample after four recrystallizations from pentane gave white crystals, mp 77–79°.

2,6-Dimethyl-2,6-*cis,trans*-cyclodecadienyl Methyl Ether.—To a slurry of 0.243 g (10.1 mmol) of pentane-washed sodium hydride oil dispersion in 1 ml of ether was added 0.385 g (2.16 mmol) of dienol **5** in 0.2 ml of ether and 0.31 ml (4.96 mmol) of methyl iodide. After refluxing for 17 hr wet ether and then water were added and the mixture was extracted with three 40-ml portions of ether. The extracts were washed with 150 ml of saturated sodium chloride solution and dried. Filtration and evaporation gave 0.415 g (99%) of a yellow oil which, upon short-path distillation at 0.1 mm and bath temperature 60–70°, gave 0.356 g (85%) of a clear oil which showed only one peak by glpc on column 1 (126°); nmr (CS_2), center of mass of multiplet in hertz downfield from tetramethylsilane (relative area) at 42°, 176 (3.0, OCH_3), 216 (1.0, H_1), 290 (0.9, H_7), 317 (1.0, H_3); at −62°, 176 (3.0, OCH_3), 209 (0.7, $H_1{}^a$), 226 (0.3, $H_1{}^s$), 280 (0.7, $H_7{}^a$), 322 (1.2, $H_3{}^a + H_3{}^s + H_7{}^s$). (Superscripts a and s refer to anti and syn conformations.) Preparative glpc gave a clear oil which, upon distillation, afforded an analytical sample.

Anal. Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 79.95; H, 11.29.

2,6-Dimethyl-2,6-*cis,trans*-cyclodecadienyl Esters. A. Acetate.—To a solution of 0.117 g (0.65 mmol) of dienol in 0.45 ml of dry pyridine was added 0.114 ml (1.12 mmol) of acetic anhydride. After standing for 13 hr the reaction mixture was diluted with 1 ml of water and then worked up, yielding 0.126 g (87%) of clear oil. Two successive short-path distillations at a bath temperature of 27–77° (0.1 mm) gave 75 mg of product: nmr (CCl_4) τ 5.20 (t, 1), 4.85 (t, 1, J = 7.5 Hz), and 4.7 (t, 1, J = 7.1 Hz).

Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.36; H, 10.07.

B. *p*-Nitrobenzoate.—To a solution of 1.475 g (8.18 mmol) of dienol **5** in 18.8 ml of dry pyridine at 0° was added 3.000 g (16.20 mmol) of *p*-nitrobenzoyl chloride. The reaction mixture was stirred for 3 hr at 0° under nitrogen. The excess acid chloride was then destroyed by adding pieces of ice. Then 250 ml of water was added and the reaction mixture was extracted with two 250-ml portions of ether. The organic extracts were washed with two 500-ml portions of 2% hydrochloric acid and 200 ml of 2% potassium carbonate and dried. Filtration and evaporation gave 2.727 g (101%) of a white solid, mp 72–76°. Repeated recrystallizations from acetone gave white crystals: mp 78–80°; nmr (CCl_4) τ 5.13 (t, 1), 4.70 (t, 1), 4.35 (t, 1); uv max (95% ethanol) 259 nm (ϵ 13,800).

Anal. Calcd for $C_{19}H_{23}NO_4$: C, 69.28; H, 7.04; N, 4.25. Found: C, 69.26; H, 6.97; N, 4.26.

Hydrolysis of *p*-nitrobenzoate with 2.5 *N* ethanolic sodium hydroxide for 1 hr at 60° led to the recovery, after sublimation, of 71% of starting alcohol **5**, mp 77–78°.

Solvolysis of 5 *p*-Nitrobenzoate.—To a mixture of 0.810 g (2.39 mmol) of **5** *p*-nitrobenzoate and 0.706 g (8.6 mmol) of anhydrous sodium acetate was added 43.0 ml of glacial acetic acid. The reaction mixture was stirred at 30° under nitrogen for 13 hr. Then 43 ml of water was added and the aqueous phase was extracted with two 200-ml portions of hexane. The organic phase was washed with 50 ml of saturated sodium chloride solution and 100 ml of 2% potassium carbonate solution and dried. Filtration and evaporation gave 0.525 g of oil in which crystals formed on standing. The solid was separated and crystallized twice from ether, giving an analytical sample of **8b**, mp 130.5–131.5°, uv max (95% ethanol) 259 nm (ϵ 13,200).[27]

Anal. Calcd for $C_{19}H_{23}NO_4$: C, 69.28; H, 7.04; N, 4.25. Found: C, 69.35; H, 7.00; N, 4.26.

A portion (0.218 g) of solid-free oil was separated into two components, with R_f values of 0.4 and 0.7, by preparative tlc using 1:9 (v/v) ether–hexane. Recovery of the faster moving component and short-path distillation from a bath at 30–40° (0.1 mm) yielded an oil, identified as olefin **7**, which was shown to be homogeneous by glpc on column 1 (130°): ir (film) 6.11 and 11.33 μ; nmr (CCl_4) τ 8.30 (CH_3), 5.37 (CH_2=), 4.52 (−CH=); molecular weight by mass spectroscopy, 162.

After recovery, the slower moving component was found to contain about 5 mol % of *p*-nitrobenzoate, which could be almost completely removed by stirring with Norit in 2-methylbutane solution. Short-path distillation from a bath at 65–110° (0.1 mm) gave an oil, identified as acetate **8a**: ir (film) 5.80 and 8.0 μ; nmr (CCl_4) τ 8.59 and 8.35 (CH_3), 8.15 (CH_3CO), and 4.6 (−CH=); molecular weight by mass spectroscopy, 222.

A portion (87 mg) of acetate was reduced with lithium aluminum hydride and the resulting alcohol was acylated with *p*-nitrobenzoyl chloride in pyridine, yielding 117 mg (94%) of crude *p*-nitrobenzoate, mp 122–126°. Crystallization afforded, with 60% recovery, material with mp 128–129°, undepressed upon admixture with *p*-nitrobenzoate isolated from solvolysis, mp 130–131°.

4,8-Dimethylazulene. Dehydrogenation of Solvolysis Products.—The total crude product, obtained from solvolysis of 0.221 g of **5** *p*-nitrobenzoate, was mixed with 0.854 g of sulfur and heated at 222° under nitrogen for 3 min. The product was extracted first with hexane and then with boiling ethanol until the extract was colorless. All solvent was removed and the purple residue was dissolved in ether, washed with three 25-ml portions of 2% aqueous potassium carbonate, and dried. Filtration and evaporation gave 35 mg of a purple solid, which was purified by two preparative tlc treatments, using hexane, which gave 21 mg of purple crystals, mp 68–70° (lit.[28] 69°), nmr (CCl_4) τ 7.15 (CH_3).

Pyrolysis of Acetate 8a.—A solution of 0.946 g (4.24 mmol) of acetate **8a** (purified by tlc) in 11.0 ml of hexane was added dropwise over 1 hr to a 1 × 34 cm tube of $^1/_8$ in. glass helices maintained at 425° and swept by a stream of dry nitrogen (flow rate 240 ml/min). Two 2-ml portions of hexane were then passed through the tube, which was then allowed to cool to 50° and rinsed with 50 ml of hexane. The combined organic fractions were washed with 50 ml of 2% aqueous potassium carbonate and dried. Filtration and evaporation gave 0.570 g (82%) of an oil which was shown to consist of two components, with retention times of 20 (47%) and 23 min (53%).

Preparative glpc afforded two fractions, the first containing 87% of the 20-min component, the second 91% of the 23-min component. Glpc of each fraction on columns 5 and 6 (150°) did not indicate the presence of a third component. The major component in the first fraction was identified as olefin **7** by comparison with solvolysis olefin (nmr spectrum and glpc coinjection). The major component in the second fraction was identified as olefin **9a** on the basis of absorptions in the nmr spectrum (CCl_4) at τ 7.47 (doubly allylic CH_2) and 4.56 (two −CH=).

2,6-Dimethyl-*trans*-bicyclo[5.3.0]deca-2,6-diene-1,7-d_2 (9b).—The preparation of this diene is given briefly as illustrative of the synthesis of deuterated compounds.

Reduction of 30.25 g (0.157 mol) of dione **1b** in ethanol with 1.660 g (0.159 equiv) of sodium borodeuteride gave, after work-up, 3.27 g (76%) of deuterated ketol **2b**, mp 85–87°. Tosylation with 45.24 g (0.238 mol) of tosyl chloride in pyridine yielded 37.42 g (90%) of deuterated keto tosylate, mp 107–109°. Epoxidation in methanol was allowed to proceed until the ratio of absorbances for the uv maxima at 228 and 245 nm was 9.5:1. Work-up gave 40 g (39.1 g theoretical) of white gum which, upon treatment with hydrazine hydrate and acetic acid in methanol, evolved nitrogen (57%) and afforded, after work-up, 38.4 g of product. Fragmentation gave 21 g of oil which was triturated with 2-methylbutane and thereby separated into 3.3 g of gummy solid and 17.7 g of brown oil. Distillation of the oil gave a total of 11.5 g (41%

(27) Based on the given uv max the yield of *p*-nitrobenzoate in the solvolysis product was calculated to be 8%. (A 5% yield of crystalline material, mp 120–125°, was recovered from one run.)

(28) Mueche, ref 11.

based on starting dione **1b**) of **4b**-7-d_1 after triturating the initial residue with 2-methylbutane, separating, distilling, and combining distillates. A 5.03-g portion of deuterated dienone was reduced with lithium aluminum deuteride, using the procedure described for the undeuterated case, and afforded 5.0 g (98%) of **5**-1,7-d_2, mp 75–77.5°. This was converted to 6.4 g (70%) of **5**-1,7-d_2 *p*-nitrobenzoate, mp 73–78°, which was solvolyzed in buffered acetic acid for 19 hr at room temperature. Work-up gave 4.09 g of product which yielded 0.36 g (5.6%) of dideuterated **8b** after addition of 2-methylbutane and filtration. The remaining oil was subjected to preparative tlc (development with 1:9 ether–hexane), giving 1.53 g of dideuterated **7** and 2.20 g of cloudy yellow oil which afforded 2.0 g of dideuterated acetate **8a** as a clear oil after treatment with Norit in 2-methylbutane (<1% *p*-nitrobenzoate present). Pyrolysis of a 0.528-g portion of acetate yielded 0.279 g (72%) of a mixture of dienes which was separated by preparative glpc on column 2 (120°) into two fractions, the second of which (69 mg) was, by analytical glpc, a 90:10 mixture of **9b** and dideuterated **7**, respectively: nmr (CCl_4) τ 7.47 (triplet of septuplets, J = 5.8 and 1.3 Hz) and 4.56 (triplet of quartets, J = 5.8 and 1.4 Hz).

Registry No.—**2b** tosylate, 30783-60-9; **4a**, 30783-61-0; **4b**, 30783-62-1; **5**, 30783-63-2; **5** methyl ether, 30783-64-3; **5** acetate, 30783-65-4; **5** *p*-nitrobenzoate, 30783-66-5; **7**, 30783-67-6; **8a**, 30783-68-7; **8b**, 30783-69-8.

Cyclopropanes. XXX. Haller–Bauer Cleavage of Phenyl Cyclopropyl Ketones[1]

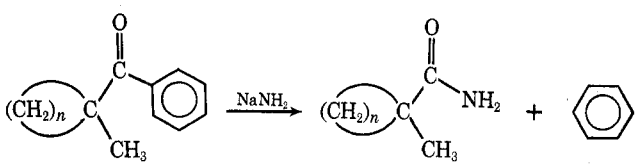
H. M. WALBORSKY,*[2] L. E. ALLEN, H.-J. TRAENCKNER, AND E. J. POWERS

Department of Chemistry, Florida State University, Tallahassee, Florida 32306

Received February 9, 1971

The syntheses and the establishment of the absolute configurations of 1-chloro-, 1-fluoro-, and 1-methoxy-2,2-diphenylcyclopropyl phenyl ketones are described. The optically active ketones were cleaved with sodium amide to yield optically active 1-chloro-, 1-fluoro-, and 1-methoxy-2,2-diphenylcyclopropane, respectively.

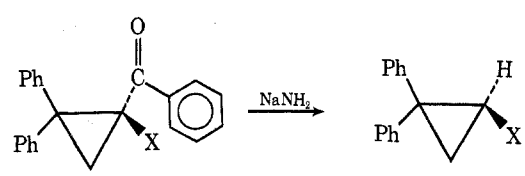
The Haller–Bauer cleavage of nonenolizable ketones such as 1-alkylcyclohexyl phenyl,[3] 1-alkylcyclopentyl phenyl,[3] 1-alkylcyclobutyl phenyl,[3] and 1-alkylcyclopropyl phenyl[4] ketones with sodium amide proceeds in the direction to produce largely the 1-alkylcycloalkanecarboxamide and benzene.



n = 2-5

A notable exception was observed in the case of 1-alkylcyclopropyl phenyl ketones in that certain 2-substituted cyclopropyl ketones such as 1-methyl-2,2-diphenylcyclopropyl phenyl ketone[5] (**1**) and *Z*-2-phenylcyclopropyl phenyl ketone[6] cleaved predominantly in the reverse manner. These observations were rationalized[6] on the basis that relief of steric interaction between the phenyl group in the 2 position and the carbonyl in the 1 position provided the driving force for the reverse cleavage.

Moreover, it was demonstrated that cleavage of **1** was stereospecific in that the hydrocarbon, 1-methyl-2,2-diphenylcyclopropane (**5**) formed by cleavage of optically active **1**, was optically pure and its configuration was retained. In connection with some other work it became necessary to prepare optically active 1-chloro-2,2-diphenylcyclopropane (**6**), 1-fluoro-2,2-diphenylcyclopropane (**7**), and 1-methoxy-2,2-diphenylcyclopropane (**8**). Based on our previous experience, the Haller–Bauer cleavage reaction seemed a promising route for accomplishing this. It was not clear, however, what the effect of an α-halo or methoxyl substituent would have on the course of the reaction.



X = CH_3 = **1**-(−)-(*R*) X = CH_3 = **5**-(+)-(*S*)
Cl = **2**-(+)-(*S*) Cl = **6**-(+)-(*S*)
F = **3**-(−)-(*S*) F = **7**-(−)-(*S*)
CH_3O = **4**-(+)-(*S*) CH_3O = **8**-(+)-(*S*)

Syntheses and Absolute Configurations.—The synthesis and absolute configuration of (−)-(*R*)-**1** has previously been described.[5] Optically active (+)-(*S*)-**2** was prepared by the addition of phenyllithium to known[7] (+)-(*S*)-1-chloro-2,2-diphenylcyclopropanecarboxylic acid. The syntheses of **3** and **4** were achieved in an analogous manner to that of **1** and **2**. This involved the addition of diazodiphenylmethane to α-fluoro and α-methoxy acrylate, which yielded after saponification the 1-fluoro- and 1-methoxy-2,2-diphenylcyclopropanecarboxylic acids, respectively. The acids were resolved using an appropriate alkaloid and the optically active acids were treated with phenyllithium to obtain **3** and **4** (see Experimental Section).

The absolute configuration of **3** was established by relating its precursor, 1-fluoro-2,2-diphenylcyclopropanecarboxylic acid, to 2,2-diphenylcyclopropanecarboxylic acid. The absolute configuration of the latter

(1) The support of this work by grants from the National Science Foundation and Public Health Service Grant No. 04065 from the National Cancer Institute is gratefully acknowledged.

(2) Address correspondence to this author.

(3) K. E. Hamlin and V. Biermacher, *J. Amer. Chem. Soc.*, **77**, 6376 (1955); for a review see K. E. Hamlin and A. W. Weston, *Org. React.*, **9**, 1 (1957).

(4) F. J. Piehl and W. G. Brown, *J. Amer. Chem. Soc.*, **75**, 5023 (1953); C. L. Bumgardner, *J. Org. Chem.*, **29**, 767 (1964).

(5) F. J. Impastato and H. M. Walborsky, *J. Amer. Chem. Soc.*, **84**, 4838 (1962); H. M. Walborsky and F. J. Impastato, *Chem. Ind. (London)*, 1690 (1958).

(6) C. L. Bumgardner and K. G. McDaniel, *J. Amer. Chem. Soc.*, **91**, 6821 (1969).

(7) H. M. Walborsky and A. E. Young, *ibid.*, **86**, 3288 (1964).