chloro-2,2-diphenylcyclopropane, $[\alpha]^{25}D$ −64.8° (*c* 1.0, $CHCl_3$), prepared from acid, $[\alpha]^{25}_{Hg}$ −82.1°, 93.9% optically pure, 150 mg of sodium amide, and 9 ml of benzene was stirred at reflux under nitrogen for 20 hr. Ice water was added and the solution was washed with water until the washings were neutral, dried, concentrated, and subjected to preparative tlc on silica gel using benzene–hexane (1:1). The band with the highest R_f value weighed 18 mg and proved to be (−)-(*R*)-1-chloro-2,2-diphenylcyclopropane based on nmr spectrum and elemental analysis: $[\alpha]^{23}_{Hg}$ −202° (*c* 0.16, $CHCl_3$); nmr (CCl_4) δ 1.71 (d, 2, *J* = 6 Hz, $-CH_2-$), 3.70 (t, 1, *J* = 6 Hz, –CHCl–), 7.37 (m, 10, phenyl).

Anal. Calcd for $C_{15}H_{13}Cl$: C, 78.80; H, 5.73. Found: C, 78.69; H, 5.69.

Cleavage of (−)-(*S*)-1-Benzoyl-1-fluoro-2,2-diphenylcyclopropane.—A mixture of 1.65 g (0.005 mol) of (−)-(*S*)-1-benzoyl-1-fluoro-2,2-diphenylcyclopropane ($[\alpha]^{25}_{Hg}$ −38°), 1 g of sodium amide, and 50 ml of toluene was stirred and refluxed for 12 hr. The reaction mixture was hydrolyzed by pouring onto ice water and the organic layer was washed with water and dried over magnesium sulfate. The solvent was removed *in vacuo* and the residue was distilled to yield 580 mg (55%) of 1-fluoro-2,2-diphenylcyclopropane whose ir and nmr spectra were identical with those of an authentic sample.[18]

Cleavage of (+)-(*S*)-1-Benzoyl-1-methoxy-2,2-diphenylcyclopropane.—A mixture of 1.1 g (0.03 mol) of ketone, 1.2 g of sodium amide, and 100 ml of xylene was stirred and refluxed for 12 hr. The reaction mixture was hydrolyzed by pouring onto ice, the organic layer was separated, washed with water, and dried over molecular sieves, and the solvent removed *in vacuo*. The residue (0.95 g) was distilled to yield 0.37 g (40%) of 1-methoxy-2,2-diphenylcyclopropane, $[\alpha]^{25}_{Hg}$ +75°. Ir and nmr spectra were identical with those of the racemic sample synthesized.

(18) C.-J. Chen, Ph.D. Dissertation, Florida State University, 1969.

Registry No.—(−)-(*R*)-2, 30724-74-4; (−)-(*S*)-3, 30724-75-5; (+)-(*S*)-4, 30724-76-6; (−)-(*R*)-6, 30724-77-7; (±)-8, 30724-78-8; (±)-A, 30788-13-7; (+)-(*R*)-A, 30724-79-9; (−)-(*S*)-A, 30745-01-8; (±)-1-methoxy-2,2-diphenylcarboxylic acid, 30724-80-2, 30724-81-3 [(±)-(*R*) isomer], 30745-02-9 [(−)-(*S*) isomer]; ethyl 1-methoxy-2,2-diphenylcyclopropanecarboxylate, 30724-82-4; (−)-(*R*)-1-methoxy-2,2-diphenylcyclopropylcarbinol, 30724-83-5; (+)-(*R*)-1-methoxy-2,2-diphenylcyclopropanecarboxaldehyde, 3074 5-03-0; ethyl (±)-1-fluoro-2,2-diphenylcyclopropanecarboxylate, 30724-84-6; (±)-1-fluoro-2,2-diphenylcyclopropanecarbinol, 30724-85-7, 30745-04-1 [(+)-(*R*) isomer]; (±)-1-fluoro-2,2-diphenylcyclopropanecarboxaldehyde, 30788-14-8; 30788-15-9 [(+)-(*R*) isomer]; (±)-1-chloro-2,2-dephenylcyclopropanecarboxladehyde, 30724-86-8, 30724-87-9 [(+)-(*S*) isomer].

The Tricyclo[5.1.0.0^{3,5}]octan-2-ols

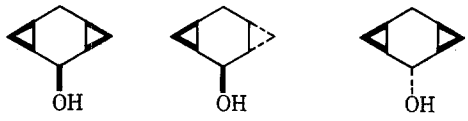
JOSEPH B. LAMBERT,* FRED R. KOENG,[1] AND J. WARREN HAMERSMA

Department of Chemistry, Northwestern University, Evanston, Illinois 60201

Received March 24, 1971

The cis,cis-, cis,trans-, and *trans,trans*-tricyclo[5.1.0.0^{3,5}]octan-2-ols have been prepared and the structures assigned by chemical correlations and nmr spectroscopy. Solvolysis of the *p*-nitrobenzoate of the cis,cis isomer has been carried out in formic acid, acetic acid, and aqueous 1,4-dioxane (85%) for kinetic and product studies. The latter two solvents produce only isomers of the starting material, but formic acid produces a complex reaction mixture that arises from cyclopropyl participation. Some solvolytic studies of the cis,trans *p*-nitrobenzoate in aqueous dioxane have been carried out.

Tricyclo[5.1.0.0^{3,5}]octan-2-ol may exist in three isomeric forms, *cis,cis*-**1** (*cc*-**1**), *cis,trans*-**1** (*ct*-**1**), and

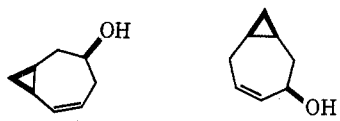


cis,cis-**1** *cis,trans*-**1** *trans,trans*-**1**

trans,trans-**1** (*tt*-**1**), from which are derived only two ketones, *cis*-**2** and *trans*-**2**. We became interested in

cis-**2** *trans*-**2**

the various isomers of **1** as solvolytic models for the related *cis*-bicyclo[5.1.0]oct-5-en-3-ol (*cis*-**3**) and *cis*-bicyclo[5.1.0]oct-4-en-3-ol (*cis*-**4**).[2] The carbonium ions from the sulfonic or carboxylic esters of **1**, **3**, and **4** are

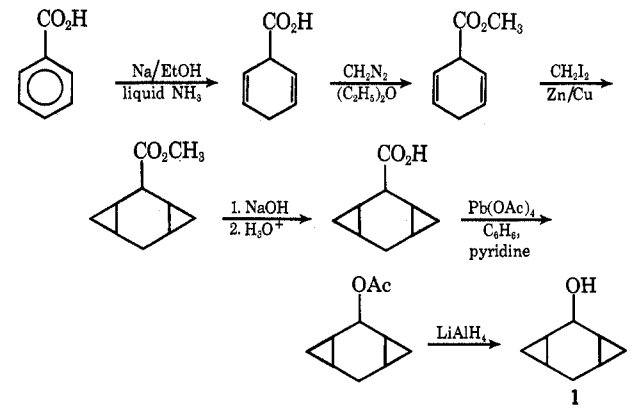


cis-**3** *cis*-**4**

valence tautomeric. We have consequently prepared each of the isomers of **1**, proved their structures, and examined the solvolytic behavior of the *p*-nitrobenzoates of *cc*-**1** and *ct*-**1**.

Synthesis and Structure.—The synthesis of *cis,cis*-**1** followed the procedures developed by Sims[3] and Winstein[4,5] (Scheme I). The stereochemistry of the Sim-

SCHEME I



1

(1) National Institutes of Health Predoctoral Fellow, 1968–1970.

(2) J. B. Lambert, J. W. Hamersma, A. P. Jovanovich, F. R. Koeng, S. A. Sweet, and P. J. Kucinski, *J. Amer. Chem. Soc.*, **92**, 6372 (1970).

(3) J. J. Sims, *ibid.*, **87**, 3511 (1965).

(4) T. Hanafusa, L. Birladeanu, and S. Winstein, *ibid.*, **87**, 3510 (1965).

(5) L. Birladeanu, T. Hanafusa, B. Johnson, and S. Winstein, *ibid.*, **88**, 2316 (1966).

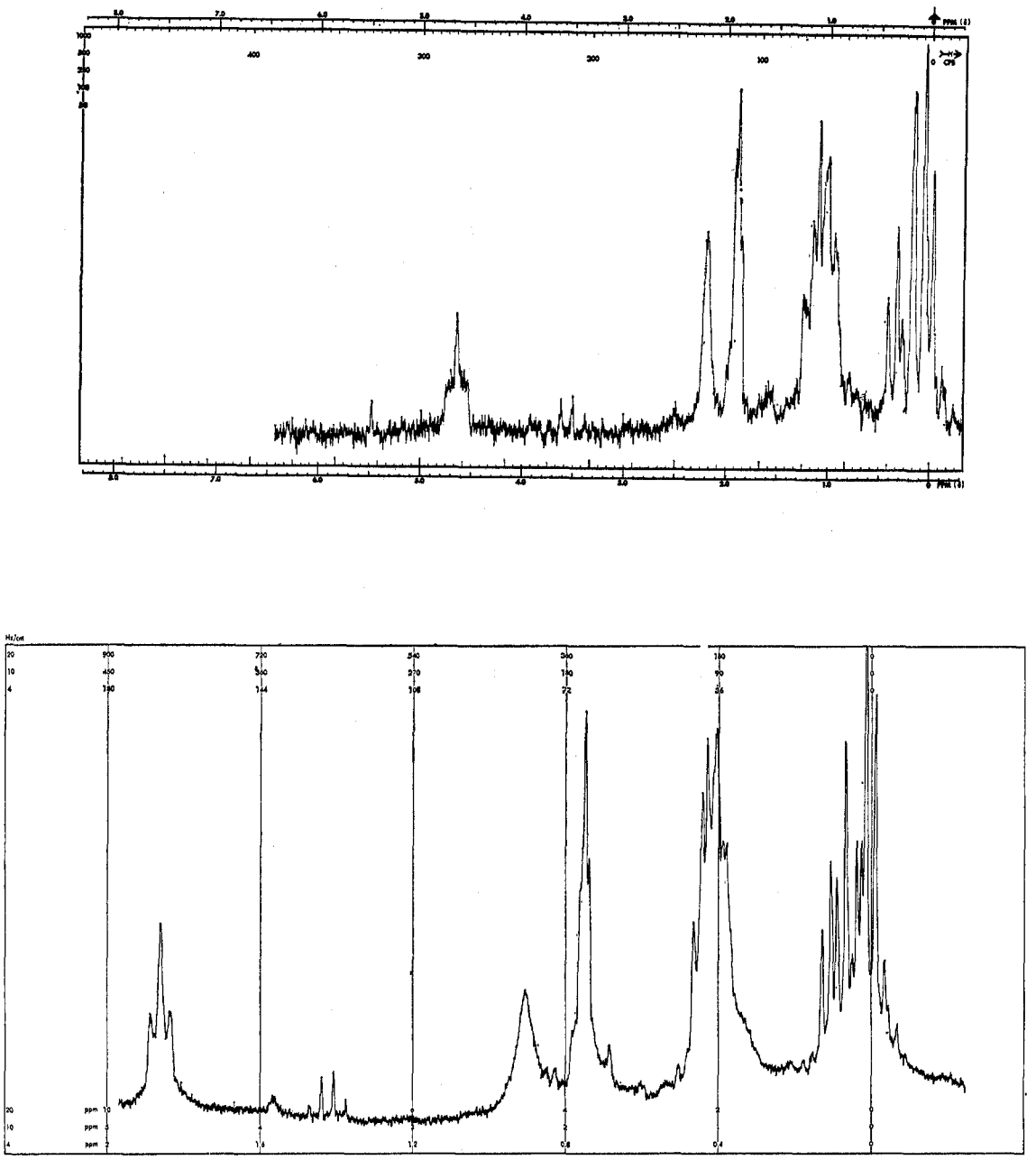


Figure 1.—The 60- (upper) and 90-MHz (lower) proton spectra of *cis,cis*-tricyclo[5.1.0.0^{3,5}]octan-2-ol in $CDCl_3$. The small quartet at δ 3.6 is due to an ethyl ether impurity. The 90-MHz spectrum is on the 10 Hz/cm scale.

mons–Smith reaction is thought to produce the cis,cis carboxylate. The corresponding acid was purified by recrystallization and converted by treatment with lead tetraacetate ultimately to the cis,cis alcohol,[3-5] which is a white, crystalline solid, mp 50–51°. Oxidation of this alcohol to the ketone *cis*-**2** and reduction with lithium aluminum hydride produced both the original alcohol, and a new alcohol, assigned the structure *tt*-**1**.

The mother liquor from purification of the cis,cis carboxylic acid was found to contain a significant amount of an isomeric acid. This mixture was carried through the reaction sequence to the alcohols **1** and thence by Jones oxidation to a mixture of two ketones **2**. These materials were separated by vpc and the new ketone was assigned the structure *trans*-**2**. Reduction of this new ketone with lithium aluminum hydride produced a single alcohol, thought to be *ct*-**1**.

The mass spectra and analytical data for *cc*-**1** and its derivatives indicate that a molecule with the correct formula is obtained from the above synthetic sequence. Although cis addition is fully expected for the Simmons–Smith reaction,[3,4,6] the stereochemistry of the lead tetraacetate oxidation is less well established. The structure of *ct*-**1** is firm, since it is the only alcohol produced from the ketone *trans*-**2**, whereas *cis*-**2** produces two alcohols, *cc*-**1** and *tt*-**1**. Stronger evidence is therefore required for differentiating the two alcohols with cis cyclopropane rings.

For further structural information we have examined the nmr spectra of the three isomers. Figure 1 shows the 60- and 90-MHz proton spectra of *cc*-**1**, and Table I summarizes the observed resonance positions of the 2 hydrogens for the three alcohols and the two *p*-nitrobenzoates.

For each isomer there are two conformational forms, given in Chart I. For *cc*-**1** and *tt*-**1**, the series B con-

(6) C. D. Poulter, E. C. Friedrich, and S. Winstein, *J. Amer. Chem. Soc.*, **91**, 6892 (1969); *ibid.*, **92**, 4274 (1970).

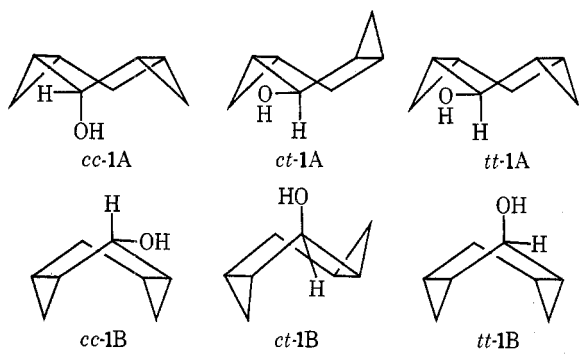
TABLE I

NMR SPECTRAL PARAMETERS

Compd	δ, ppm[a]	J, Hz[b]
cc-1	4.65 (t)	6.0
ct-1	4.14 (d of d)	6.5
		2.3
tt-1	3.92 (broad s)	
cc-1-OPNB	6.15 (t)	6.5
ct-1-OPNB	5.48 (d of d)	6.0
		2.3

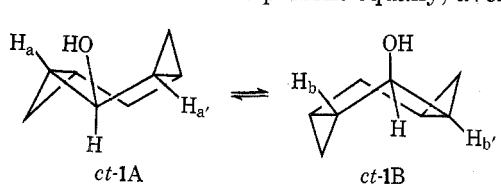
[a] The chemical shift of the 2 proton downfield from TMS. [b] The coupling constant between the 2 proton and the protons on adjacent carbon atoms.

CHART I



formers are clearly less stable than the series A conformers, because of nonbonded repulsions between the opposed cyclopropane hydrogens. The series B conformer of *ct*-1 is also probably the less stable because it would place the hydroxyl group in the very crowded "flagpole" position. An examination of the more stable A conformers indicates that the 2 hydrogen should be increasingly shielded by the cyclopropane rings in the order *cc*, *ct*, *tt*. In *cc*-1, this proton is directed away from both cyclopropane rings and is therefore least affected. In *ct*-1 the 2 proton is situated over the face of one cyclopropane ring, and in *tt*-1 this proton is over both rings. The region in space above a cyclopropane ring is well known to be shielding.[7] The alcohol with the most shielded proton, resonating at δ 3.92, must therefore be *tt*-1. Similarly, the δ 4.65 isomer must be *cc*-1, and the δ 4.14 isomer *ct*-1. These assignments are in accord with the chemical evidence presented above.

Further structural verification may be obtained from the vicinal coupling constants of the proton at the 2 position. The isomer *ct*-1 (δ 4.14) is easily identified by the four-line pattern of the 2 proton coupled to nonequivalent vicinal protons. In *cc*-1 and *tt*-1, the vicinal couplings must be equal because of the plane of symmetry passing through C-2 and C-6. In conformer B of *ct*-1, the larger coupling (6.5 Hz) is most likely associated with the adjacent proton that is almost eclipsed ($H_{b'}$) and the smaller coupling (2.3 Hz) with the staggered proton (H_b). Similar values are expected from conformer A. If A and B were present equally, averaging

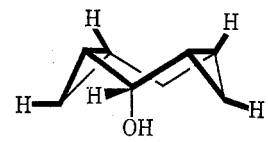


ct-1A *ct*-1B

(7) J. B. Lambert, J. L. Gosnell, Jr., D. S. Bailey, and L. G. Greifenstein, *Chem. Commun.*, 1004 (1970).

of the couplings would result in a simple triplet splitting. The observed four-line pattern indicates that one conformer, presumably A, must predominate.

The 2 proton in *cc*-1 (δ 4.65) is equivalently coupled to the two vicinal protons to give a triplet (^3J = 6.0 Hz). This coupling corresponds to the larger coupling constant in *ct*-1, since the coupled protons are nearly eclipsed in conformer A. The observed components of the triplet in *cc*-1 are considerably broadened with respect to the *ct*-1 peaks, most likely because of four W-path couplings over four bonds. Finally, the coupling in *tt*-1 (δ 3.92) corresponds to the smaller coupling in *ct*-1, as expected for the staggered arrangement in conformer A. The small magnitude of this coupling gives rise to only a single, broad line. The chemical evidence, the shielding of the 2 proton, and the vicinal couplings of the 2 proton thus all give identical structural assignments.



Solvolysis Results.—Although the tosylate of *cc*-1 could not be prepared by either of the most common methods,[8,9] no problems were encountered in obtaining the *p*-nitrobenzoate. The crowded environment about the hydroxyl group may preclude introduction of the tetrahedral sulfonate group but still permit the trigonal carboxylate group.

Titrimetric solvolysis rates for *cc*-1-OPNB were measured in 85% (by volume) aqueous 1,4-dioxane by the aliquot method. Infinity titers agreed well with the calculated values, so that internal return to a less reactive species is ruled out. The kinetic data are given in Table II and the activation parameters in Table III.[10]

TABLE II

KINETIC DATA FOR THE HYDROLYSIS OF *cis,cis*-1 *p*-NITROBENZOATE IN 85% DIOXANE-WATER

Temp, °C	k, sec^{-1} × 10^5	Correlation coeff
25.15	2.89	0.997
	2.62	0.998
32.25	6.43	0.998
	6.04	0.997
40.35	15.0	0.997
	14.5	0.999

TABLE III

ACTIVATION PARAMETERS (25°) FOR THE HYDROLYSIS OF *cis,cis*-1 *p*-NITROBENZOATE

E_a	20.5 ± 0.5[a]
Log A	10.5 ± 0.4[a]
$\Delta H^{\pm}$	19.9 ± 0.5[a]
$\Delta S^{\pm}$	−12.6 ± 1.7 eu
$\Delta G^{\pm}$	23.7 ± 0.7[a]
Correlation coefficient	0.999

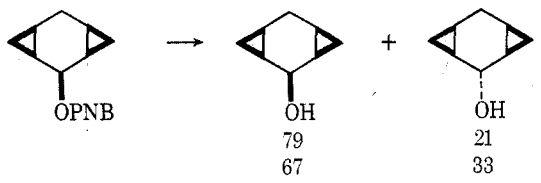
[a] Kcal/mol.

Solvolysis products were examined after 5 half-lives in dioxane–water. For the reactions in acetic acid and

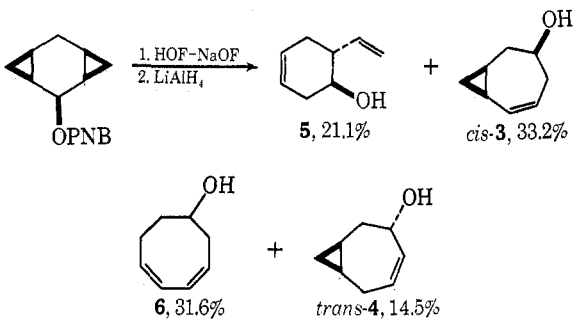
(8) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).
(9) R. M. Coates and J. P. Chen, *Tetrahedron Lett.*, 2705 (1969).
(10) A rate constant of 2.4 × 10^{-4} sec^{-1} at 25° has been quoted for the solvolysis of *cc*-1-OPNB in 80% aqueous acetone; see ref 5.

formic acid, 1.1 equiv of sodium acetate and sodium formate, respectively, were added for product studies. Completion of reaction was ascertained by infrared analysis of the product mixture for absence of nitro and benzoate bands. All the products were subjected to the reaction conditions and found to be stable. In formolysis and acetolysis, the esters products were reduced to the alcohols for analysis. The three alcohols **1** are destroyed under most gas chromatographic conditions but survive a 6 ft × 1/8 in. 10% SE-30 column without alteration, eluting in the order *ct*, *tt*, *cc*. The alcohol products were oxidized by the Jones procedure as a cross check, and the ketones were analyzed by gas chromatography, with *trans*-**2** at the shorter retention time.

The only products from the hydrolysis and the acetolysis of *cc*-**1**-OPNB were *cc*-**1** and *tt*-**1** in slightly differing



proportions. Four products were obtained from solvolysis in the less nucleophilic formic acid: *trans*-2-vinylcyclohex-4-enol (**5**), *cis*-bicyclo[5.1.0]oct-5-en-3-ol



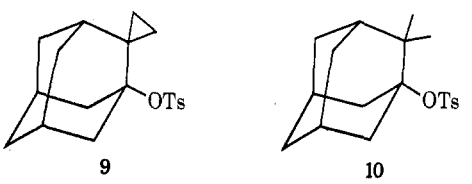
(*cis*-**3**), cycloocta-3,5-dienol (**6**), and *trans*-bicyclo[5.1.0]oct-4-en-3-ol (*trans*-**4**). The structure proofs are given in the Experimental Section. Specifically excluded as formolysis products by comparison of vpc retention times with those of authentic materials were all the tricyclic alcohols **1**, as well as *trans*-**3** and *cis*-**4**. The vinylcyclohexenol **5** is the end product under isomerizing conditions (trifluoroacetolysis or unbuffered formalysis after extended reaction times).

The *p*-nitrobenzoate of *ct*-**1** was solvolyzed in 85% dioxane–water and found to yield only *ct*-**1**. Formolysis gave several products, none of which were **1**, **3**, or **4**. These reactions were not examined further.

Discussion

The ability of a cyclopropane ring to conjugate with a developing positive charge is critically dependent on the geometry of the system. The interaction is maximized in the bisected geometry (**7**) and reduced in the parallel geometry (**8**).[11] The geometrical requirement for

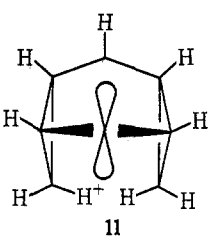
cyclopropylcarbinyl participation is that one cyclopropyl carbon–carbon bond be anti periplanar to the leaving group. Under these conditions the bisected structure is easily obtained. The adamantane system **9** is an example of a molecule in which there is no cyclopropyl bond anti periplanar to the tosylate group; so an ion of the type **8** results.[12] As a consequence, **9** solvolyzes



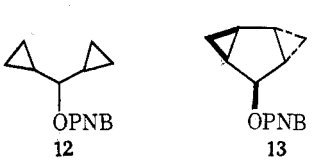
over a thousand times as slowly as **10**. Thus, in the absence of conjugative assistance, a cyclopropane ring can severely retard the rate of solvolysis.

Examination of molecular models shows that the stable conformer of *cc*-**1**-OPNB (A in Chart I) does not contain the requisite anti-periplanar arrangement for participation. The less stable conformer (B), however, contains one such bond in each cyclopropane ring. This conformer is therefore expected to be solvolytically more reactive. Similar analysis shows that *tt*-**1**-OPNB and *ct*-**1**-OPNB have anti-periplanar arrangements with both cyclopropane rings in the more stable conformer (A) and should therefore be able to react without a prior conformational interconversion.

The ion that results from the solvolysis of *cc*-**1**-OPNB might have the structure **11**, in which both cyclopropane



rings enjoy the bisected geometry. The hydrolysis reaction occurs some 20–30 times as rapidly as that of dicyclopropylcarbinyl *p*-nitrobenzoate (**12**),[13] which is



conformationally much more flexible and which cannot attain the ideal geometry of **11** because of steric factors. The five-membered analog **13** furnishes an interesting contrast to **1**. The cyclopropyl bonds are no longer anti periplanar to the leaving group because of the constraints of the cyclopentane ring; so this molecule hydrolyzes considerably more slowly than **12**.[14]

(11) C. V. Pittman, Jr., and G. Olah, *J. Amer. Chem. Soc.*, **87**, 2998 (1966).

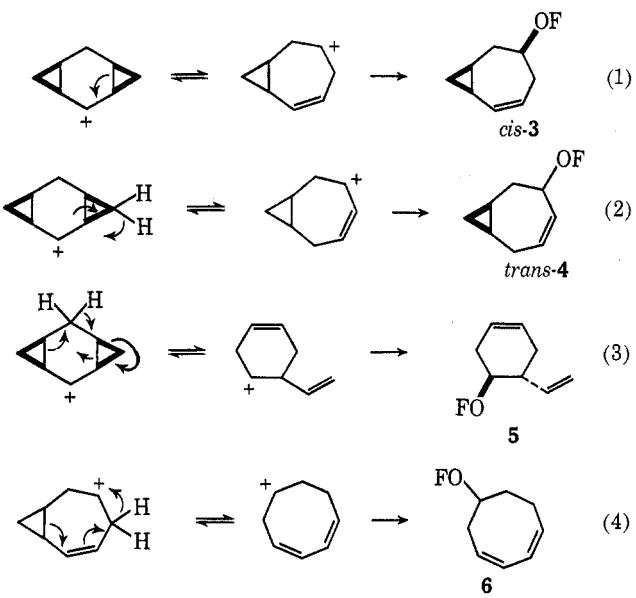
(12) B. R. Ree and J. C. Martin, *ibid.*, **92**, 1660 (1970).

(13) A. P. Krapcho, R. C. H. Peters, and J.-M. Conia, *Tetrahedron Lett.*, 4827 (1968).

(14) J. J. Gajewski and C. N. Shih, *ibid.*, 2967 (1970).

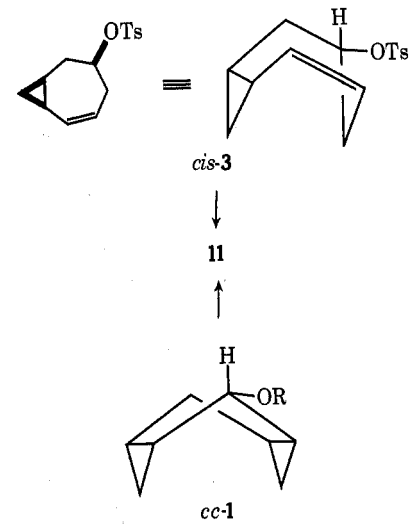
Although the large rate acceleration in *cc*-1-OPNB is indicative of significant cyclopropyl participation, the stereochemistry of the products is less easy to interpret. The major product of both hydrolysis and acetolysis is cc-1, the starting material with retained stereochemistry. In addition, both reactions produce some of the inverted isomer, *tt*-1. It is not possible to decide if this latter material arises from a k_s (nucleophilic displacement by solvent) component of the rate or if the ion **11** gives both products. The similarity of isomer ratios in acetic acid and dioxane–water, solvents of extremely different nucleophilicities, suggests that the k_s interpretation is unlikely.

In the more strongly ionizing, less nucleophilic medium offered by formic acid, carbonium ion intermediates are longer lived and hence more prone to rearrange. Thus, formolysis yields a complex reaction mixture. The major product (*cis*-**3**) is the result of a cyclopropylcarbinyl–allylcarbinyl rearrangement (eq 1). The remaining products probably arise from hydride-shift processes, as suggested in eq 2–4, which are by no means intended to be definitive mechanisms. Vinyl products analogous to **5** have been observed in other cyclopropylcarbinyl systems.[15]



Solvolysis of *cis*-**3**-OTs with double bond participation can lead to the same ion as from *cc*-**1**, since the two materials are conformationally identical (eq 5). In the illustrated conformation of *cis*-**3** (eq 5), the cyclopropane ring is incorrectly oriented for participation, but the double bond is correctly oriented.[2] Formolysis of *cis*-**3**-OTs produces[2] *cis*-**3**, *trans*-**4**, **5**, and **6** in almost the same proportions as does *cc*-**1**-OPNB. All evidence points to a near identity of ions from the two sources.

In summary, we have prepared the three isomers of tricyclo[5.1.0.0^{3,5}]octan-2-ol (**1**) and proved their structures. Hydrolysis and acetolysis of the *p*-nitrobenzoate of the cis,cis isomer produce only the two isomers of **1** in which the cyclopropane rings remain cis. Intermediate carbonium ions do not therefore undergo conformational or geometrical isomerization to an arrangement with the cyclopropane rings trans. Furthermore, hydrolysis of the cis,trans *p*-nitrobenzoate yields only



material with the rings still trans to each other. The kinetics of hydrolysis of *cis,cis*-**1**-OPNB implicate strong anchimeric assistance from at least one of the cyclopropane rings. Examination of the two available conformations indicates that solvolysis occurs from the less stable form. This conformation is expected to give an ion very similar to that produced by double bond participation in *cis*-bicyclo[5.1.0]oct-5-en-3-yl tosylate (*cis*-**3**-OTs). In fact, formolysis of *cis*-**3**-OTs gives all the products observed in the formolysis of *cis,cis*-**1**-OPNB, and in the same proportion. This similarity of product distribution is taken as evidence that the intermediate carbonium ions have similar or even identical structures.

Experimental Section

All melting points were measured on a Fisher-Johns apparatus and have been left uncorrected. The infrared spectra were measured on a Beckman IR-5 infrared spectrometer. Ultraviolet spectra were measured on a Cary 14 recording spectrophotometer. Routine nmr spectra were taken on Varian Associates A-60 and T-60 spectrometers. The nmr spectrum of *cc*-**1** was also measured on a Bruker HFX-10 90-MHz spectrometer. Chemical shifts are reported in parts per million downfield from tetramethylsilane. Coupling constants are reported in hertz. A Consolidated Electrodynamics Corp. 21-104 mass spectrometer was used for the mass spectral work. Analytical vapor phase chromatography data were obtained with either a Hewlett-Packard Model 700 chromatograph or a Varian Associates Aerograph Series 1520B. Preparative vpc work was performed on the Hewlett-Packard chromatograph. Elemental analyses were performed by Micro-Tech Laboratories, Inc., Skokie, Ill.

1,4-Dihydrobenzoic Acid.—To a 5-l., three-necked flask, equipped with a mechanical stirrer, a Dry Ice–acetone condenser, and a gas-inlet tube, was added 500 ml of anhydrous ethanol and 60 g (0.49 mol) of benzoic acid. Approximately 3 l. of ammonia was distilled into the flask. While the solution was being stirred, 37 g (1.6 g-atoms) of sodium was added gradually. The blue color of the sodium–ammonia solution was allowed to disappear before each new addition of sodium. When all of the sodium had been consumed, 87.5 g (1.65 mol) of NH_4Cl was added. The mixture was stirred and then allowed to stand until the ammonia had evaporated. The reaction mixture was worked up by dissolving the contents of the flask in ice water and acidifying the solution with concentrated HCl. The aqueous solution was extracted five times with 200-ml portions of ether. The extracts were combined and dried over $MgSO_4$, filtered, and stripped of solvent, to give 57.4 g of the acid.

Methyl 1,4-Dihydrobenzoate.—Diazomethane was prepared by the gradual addition of 75.6 g (0.73 mol) of *N*-methyl-*N*-nitrosourea[16] to a stirred system of 330 g of 40% potassium hy-

(15) K. B. Wiberg and J. G. Pfeiffer, *J. Amer. Chem. Soc.*, **92**, 553 (1970).

(16) F. Arndt, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 461.

TABLE IV
NUCLEAR MAGNETIC RESONANCE DATA

Compd	Cyclopropane ring	$-CH_2-$	CH–O	OH	Aromatic
cis-2	1.56 (m, 4), 0.80 (m, 4)	2.08 (m, 2)			
cis,cis-1	1.07 (m, 4), 0.16 (m, 4)	1.90 (m, 2)	4.65 (t, 1, J = 6.0 Hz)	2.20 (s, 1)	
cis,cis-1-OPNB	1.40 (m, 4), 0.55 (m, 4)	2.13 (m, 2)	6.15 (t, 1, J = 6.5 Hz)		8.18 (m, 4)
trans-2	1.50 (m, 6), 0.82 (m, 2)	2.32 (m, 2)			
cis,trans-1	0.60 (m, 7), −0.12 (m, 1)	1.63 (m, 2)	4.14 (q, 1, J = 6.5, J = 2.3 Hz)	3.06 (s, 1)	
cis,trans-1-OPNB	0.60 (m, 8)	1.80 (m, 2)	5.48 (q, 1, J = 6.0, J = 2.3 Hz)		8.17 (m, 4)

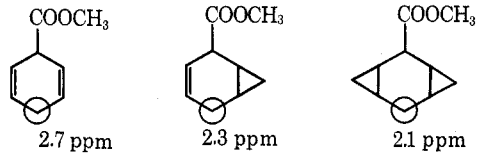
droxide under 1200 ml of ether at 0°. The development of a yellow color in the ether layer indicated the presence of diazomethane. The mixture was stirred for 1.5 hr and then the ether layer was decanted. The ether–diazomethane solution was dried 1 hr over KOH before use.

An ether solution of 1,4-dihydrobenzoic acid was prepared by dissolving 57.5 g (0.46 mol) of the acid in 1 l. of ether, drying the solution over $MgSO_4$, and filtering. The ether–diazomethane solution was added to the filtered solution of the acid until the yellow color of diazomethane persisted. The excess was destroyed by the addition of acetic acid. The ether was removed and the product distilled under vacuum to give 56.4 g of product or 82% from benzoic acid, bp 33° (0.5 mm).

Zinc–Copper Couple.—Zinc dust (50 g) was placed in a sintered-glass funnel. The zinc dust was slurried with and then filtered from each of the following solutions: four times with 40-ml portions of 3% HCl solution, five times with 100-ml portions of water, two times with 75-ml portions of 2% copper sulfate solution, five times with 100-ml portions of water, and five times with 100-ml portions of anhydrous ether. The zinc–copper couple was air-dried a few minutes in the funnel and then dried overnight in a vacuum desiccator.

Methyl Tricyclo[5.1.0.0^{3,5}]octyl-2-carboxylate.—To a 2-l., three-necked flask equipped with a mechanical stirrer, an addition funnel, and a condenser, were added 93.5 g (1.4 mol) of zinc–copper couple, 750 ml of ether, and approximately 1/2 of 344 g (1.3 mol) of methylene iodide. This solution was brought to reflux with stirring in order to initiate the formation of the Simmons–Smith reagent. When the solution was refluxing gently with no further heating, the remainder of the methylene iodide was added in order to maintain the reflux action. The solution was allowed to reflux for 1 hr after the complete addition of the methylene iodide. At this time 55.7 g (0.40 mol) of methyl 1,4-dihydrobenzoate was added slowly. Refluxing was continued for 8 hr. The reaction mixture was cooled, filtered, and worked up by washing with the following solutions: three times with 100-ml portions of saturated NH_4Cl solution, three times with 100-ml portions of saturated $NaHCO_3$ solution, and three times with 100-ml portions of saturated NaCl solution. The ether solution was dried over $MgSO_4$, filtered, and stripped of solvent. The residue was used directly in the repeated treatments with Simmons–Smith reagent.

The above reaction was repeated two additional times using 250 g of methylene iodide and 75 g of zinc–copper couple to ensure diaddition of the Simmons–Smith reagent. After the third Simmons–Smith treatment, the product was distilled under vacuum. Careful distillation of the product and examination of the fractions by nmr made it possible to obtain a fairly pure diaddition product. The distinguishing nmr data are given.



The optimum yield of nearly pure diaddition product was 27.0 g (40%), bp 45° (0.5 mm).

Tricyclo[5.1.0.0^{3,5}]octyl-2-carboxylic acid was prepared by refluxing 27.0 g (0.16 mol) of the above ester with 575 g of 10% aqueous NaOH solution for 3 hr. The aqueous solution was cooled, acidified with concentrated HCl, and extracted with ether. The ether solution was dried over $MgSO_4$ and filtered, and the ether was removed to give 18.5 g (75%) of the acid. The crude acid was recrystallized from pentane to give 11.4 g of pure cis,cis acid, mp 105–106° (lit.[3] mp 106–107°).

***cis,cis*-Tricyclo[5.1.0.0^{3,5}]oct-2-yl Acetate** (*cis,cis*-1-OAc).—In a three-necked, 500-ml flask equipped with a condenser, a nitrogen-inlet tube, and a stirrer, were placed 11.3 g of the cis,cis acid (0.073 mol), 9 ml of dry pyridine (distilled first from tosyl chloride, then from calcium hydride, and stored over molecular sieves), and 230 ml of dry benzene. The system was flushed with nitrogen. Lead tetraacetate (50 g) was stirred into the mixture, which was slowly brought up to reflux and kept there for 1 hr. A heavy white precipitate of lead diacetate formed during the reaction. The reaction mixture was cooled and filtered. The benzene filtrate was washed with water, 1 N NaOH solution, water, 1 N HCl solution, and water. The organic phase was dried over $MgSO_4$, filtered, and distilled to give 9 g (73%) of *cis,cis*-1-OAc: bp 55° (0.1 mm); ir 3100 (w), 3030 (m), 2820 (m), 2720 (w), 1735 (s), 1375 (s), 1250 (s), 1030 (s), 1005 (s), 957 (s), 870 (m), 845 (w), and 780 cm^{-1} (w); nmr δ 5.8 (t, 1, CHOAc), 2.0 (s, 3, CH_3), 1.1 (six-membered-ring protons), and 0.3 (m, 4, cyclopropane ring CH_2).

***cis,cis*-Tricyclo[5.1.0.0^{3,5}]octan-2-ol** (*cis,cis*-1).—To a 200-ml three-necked flask equipped with a condenser, an addition funnel, and a stirrer was added 1.3 g (33 mmol) of lithium aluminum hydride and 100 ml of anhydrous ether. To this stirred solution was added 5.3 g (33 mmol) of *cis,cis*-1-OAc in 50 ml of ether at a rate suitable to maintain reflux. At the end of the addition the solution was heated and held at reflux temperature for 30 min. The reaction mixture was hydrolyzed by the careful addition of 4.9 ml of 5% sodium hydroxide solution. When the solids in the flask had turned white, the mixture was filtered. The solids were returned to the flask and boiled with tetrahydrofuran. Again the solution was filtered, and the tetrahydrofuran treatment repeated. The filtrates were combined, dried over $MgSO_4$, filtered, and stripped of solvent. The yield of crude product was 3.5 g (90%). The product was recrystallized from pentane to give a white crystalline material, mp 50–51°. Table IV summarizes the nmr spectral data for *cis,cis*-1 and its derivatives: ir (CCl_4) 3400 (s), 3080 (m), 2980 (s), 2790 (s), and 2680 cm^{-1} (s). *Anal.* Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74; O, 12.88. Found: C, 77.23; H, 9.45; O, 12.66.

***cis,trans*-Tricyclo[5.1.0.0^{3,5}]octan-2-ol** (*cis,trans*-1).—The crude acid remaining after recrystallization of the cis,cis acid was oxidized with lead tetraacetate, as described in the preparation of *cis,cis*-1-OAc. The crude acid (11.3 g) gave 5.2 g of 1-OAc (mixture of cis,cis and cis,trans). This mixture was reduced with lithium aluminum hydride by the usual procedure to give the alcohols. The alcohol mixture was oxidized in acetone by adding Jones reagent until an excess was noted by the persistence of the yellow color. The excess was destroyed by the addition of isopropyl alcohol. Water was added to the reaction mixture to dissolve all the inorganic precipitate and the resulting aqueous solution was extracted five times with ether. The ether extracts were combined, dried over $MgSO_4$, filtered, and stripped of solvent. The resulting mixture of ketones was found to be approximately 75% *cis*-2 and 26% *trans*-2 by vpc (6 ft × 1/8 in. 10% silicone rubber on Chromosorb W column at 100°, 30 ml/min). Some of the cis ketone was removed by recrystallization

from pentane. The remaining 50–50 mixture of ketones was separated by preparative vpc (10 ft × 0.5 in. 10% SE-30 silicone rubber on Chromosorb G). The yield of *trans*-**2** was 175 mg.

The *trans*-**2** was reduced with lithium aluminum hydride by the usual procedure to give *cis,trans*-**1**. Compound *cis*-**2** was also reduced to give a mixture of 45% *trans,trans*-**1** and 55% *cis,cis*-**1**. The carbonyl absorption bands for *cis*-**2** and *trans*-**2** were 1670 and 1690 cm^{-1}, respectively. *Anal.* Calcd for $C_8H_{10}O$ (*cis*-**2**): C, 78.65; H, 8.25; O, 13.10. Found: C, 78.50; H, 8.26; O, 13.18.

***cis,cis*-Tricyclo[5.1.0.0^{3,5}]oct-2-yl *p*-Nitrobenzoate (*cis,cis*-1-OPNB).**—A sample of *cis,cis*-**1** (2.28 g, 18 mmol) in 10 ml of dry pyridine was added to a solution of 4.0 g (22 mmol) of *p*-nitrobenzoyl chloride in 40 ml of pyridine. The reaction mixture was cooled in an ice bath and stirred for 2 hr. The mixture was poured into ice water and the aqueous phase was extracted with pentane. The pentane extracts were combined and dried over $MgSO_4$, filtered, and stripped of solvent. The residue was recrystallized from pentane to give 3.9 g (80%) of product: mp 45–47°; ir (CCl_4) 3100 (w), 2940 (w), 2880 (w), 2760 (w), 1725 (s), 1615 (m), and 1275 cm^{-1} (m). *Anal.* Calcd for $C_{15}H_{15}NO_4$: C, 65.93; H, 5.53; O, 23.42. Found: C, 66.10; H, 5.53; O, 23.39.

Solvolysis of Tricyclo[5.1.0.0^{3,5}]oct-2-yl *p*-Nitrobenzoate. Kinetic Studies.—The rate of solvolysis of *cis,cis*-**1**-*p*-nitrobenzoate was measured in 85% dioxane–water (by volume). The 1,4-dioxane was refluxed over sodium for 24 hr and then distilled before use. The solvolysis solvent was prepared by diluting the dioxane with water that had been deionized and distilled through a glass apparatus. A standard solution of *cis,cis*-**1**-*p*-nitrobenzoate (0.01 *M*) in the solvolysis solvent was prepared for each kinetic run and equilibrated in a constant temperature bath. Aliquots were withdrawn at intervals, quenched in dioxane, and titrated with 0.01 *M* aqueous NaOH to the bromthymol blue end point (yellow to blue).

Product Studies.—For product studies, 0.1 *M* solutions of *cis,cis*-**1**-*p*-nitrobenzoate were prepared and stirred at a predetermined temperature for various time periods. The acetolysis and formolysis reactions contained 1.1 equiv of sodium acetate and sodium formate, respectively. The solvolysis mixture was then poured into ice water and extracted several times with ether. The ether extracts were combined, washed with saturated aqueous $NaHCO_3$ solution, dried over $MgSO_4$, filtered, and stripped of solvent. Recovered ester after 1 half-life contained only *cis,cis*-**1**-*p*-nitrobenzoate.

The aqueous dioxane solvolysis products were analyzed directly on a 10% SE-30 silicone rubber on Chromosorb W column (6 ft × 1/8 in.). The alcohols were oxidized to a single ketone (*cis*-**2**) with Jones reagent.

The acetolysis products were reduced with lithium aluminum hydride and then analyzed by the same procedure used in the hydrolysis experiments. A single ketone (*cis*-**2**) was formed on oxidation.

The formolysis products were reduced with lithium aluminum hydride, hydrogenated over platinum catalyst at atmospheric pressure, and then oxidized with Jones reagent. Each step was followed by vpc analysis using a 20 ft × 1/8 in. 12% Carbowax on Chromosorb G column at 170° (30 ml/min flow rate).

Structure Proofs of Formolysis Products.—Four products were obtained from the formolysis of *cis,cis*-**1**-OPNB. Each could be obtained in a pure state by preparative vpc.

First Component.—Hydrogenation of the alcohol took up 2 mol of H_2 and produced *trans*-2-ethylcyclohexanol, which was identified by comparison with authentic samples. The nmr spectrum of the original material contained five alkenic protons and no ethyl resonances. A vinyl group is therefore present, plus one endocyclic double bond. The latter functionality was placed in the 4 position on the basis of the nmr spectrum. This component therefore has the structure *trans*-2-vinylcyclohex-4-enol.

Second Component.—An nmr spectrum of this material was identical with an authentic sample of *cis*-bicyclo[5.1.0]oct-5-en-3-ol.[17] A sample of the trans isomer was available for comparison; the reaction mixture contained only *cis*-**3**.

Third Component.—Hydrogenation of the alcohol produced cyclooctanol, with an uptake of 2 mol of H_2. The formate had an ultraviolet absorption at 225 nm (ϵ 2800), so the double bonds must be conjugated. The alcohol was oxidized to the corresponding cyclooctadienone, which had no new uv absorptions. The ketone is therefore not α,β unsaturated. Only cycloocta-3,5-dienol (**6**) has these properties.

Fourth Component.—Hydrogenation and Jones oxidation produced bicyclo[5.1.0]octan-3-one.[17] The intermediate saturated alcohol was not identical with the saturated cis alcohol from *cis*-**3**; so the stereochemistry must be trans. Furthermore, this component was different from *trans*-**3** but produced the same saturated alcohol on hydrogenation. The alkenic region of the nmr spectrum contained a two-proton AB quartet with further fine structure. The spectrum and the chemical evidence are only consistent with *trans*-bicyclo[5.1.0]oct-4-en-3-ol (*trans*-**4**).

Registry No.—*cis,cis*-**1**, 30953-03-8; *cis,cis*-**1**-OAc, 30953-05-0; *cis,cis*-**1**-OPNB, 30953-04-9; *cis,trans*-**1**, 30953-06-1; *cis,trans*-**1**-OPNB, 30883-12-6; *trans,trans*-**1**, 30889-17-9; *cis*-**2**, 30889-18-0; *trans*-**2**, 30889-19-1; methyl 1,4-dihydrobenzoate, 30889-20-4; methyl ticyclo[5.1.0.0^{3,5}]octyl-2-carboxylate, 30889-21-5.

Acknowledgments.—This work was supported by the Petroleum Research Fund, administered by the American Chemical Society (Grant 2970-AC4, 5), and by the National Science Foundation (Grants GP-9257 and GP-22942).

(17) Authentic samples of this material were made available by Dr. A. P. Jovanovich.[2]