the mass spectrum of the mixture exhibited the following abundant peaks: *m/e* (rel intensity) 202 (82), 187 (100), 145 (34), 131 (23), 57 (81), and 41 (21). These spectroscopic properties are consistent with the formulation of these by-products (mol wt 202) as various double-bond isomers formed by dehydration of the alcohol **7** during the GLC analysis and separation.

Reduction of the Octalone 8 with the CuH–*t*-BuC≡CLi Reagent. The CuH, from 1.44 g (10.0 mmol) of CuBr and 11 mmol of *i*-Bu_2AlH in 12.4 ml of heptane, was dissolved in a cold (−40 to −78°) solution of 3.85 mmol of *t*-BuC≡CLi in 18 ml of THF and the resulting cold (−27°) solution was treated with a solution of 254 mg (1.69 mmol) of the octalone **8** in 3 ml of THF. The resulting solution was stirred at −27° for 10 hr and then allowed to warm to 0° and subjected to the previously described isolation procedure. The crude neutral product was mixed with 28.0 mg of *n*-$C_{14}H_{30}$ (an internal standard) and subjected to analysis (GLC, Apiezon L on Chromosorb P) employing equipment that had been calibrated with known mixtures of authentic samples. The reaction product contained *n*-$C_{14}H_{30}$ (retention time 11.5 min), the trans ketone **10** (16.9 min, yield 5%), the cis ketone **9** (19.0 min, yield 34%), and the starting ketone **8** (33.0 min, recovery 46%). Collected (GLC) samples of each of the ketone products **9** and **10** were identified with an authentic sample by comparison of ir and mass spectra and GLC retention times.

Registry No.—**3**, 78-59-1; **7**, 53783-16-7; **8**, 1196-55-0; $(CuH)_n$, 53783-17-8; *t*-BuC≡CLi, 37892-71-0; *t*-BuC≡CLi$(CuH)_3$, 53849-09-5.

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Stereoselectivity in the Base-Catalyzed Decarboxylation of 4-*tert*-Butylcyclohexane-1,1-dioic Acid[1]

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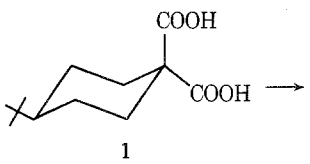
We recently reported the results of an investigation of the stereoselectivity of base-catalyzed decarboxylation of 5,5-dicarboxy-2-isopropyl-1,3-dioxane.[2] The product composition was found to be quite sensitive to the basic solvent chosen for the reaction. We were puzzled, however, by the apparent lack of sensitivity of the product composition in decarboxylation of 4-phenylcyclohexane-1,1-dioic acid to the solvent; 2,4,6-trimethylpyridine and 1,3,5-trimethylbenzene gave essentially the same result.[3] This prompted us to synthesize 4-*tert*-butylcyclohexane-1,1-dioic acid (**1**), study the diastereomeric composition of the product using a number of basic solvents, and compare these results to those of the 1,3-dioxane system.

Table I
Product Composition in the Decarboxylation of 4-*tert*-Butylcyclohexane-1,1-dioic Acid

Solvent	% 2 at 100.0°
Pyridine	70.7 ± 0.5[a]
2-Methylpyridine	70.3 ± 0.5
2,6-Dimethylpyridine	77.3 ± 0.6
N,N-Dimethylaniline	72.4 ± 0.6
N,N-Dimethylformamide	69.1 ± 1.3

[a] All errors are standard deviations.



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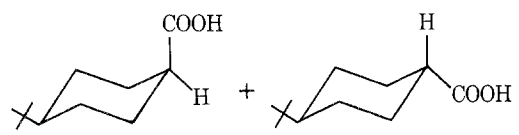
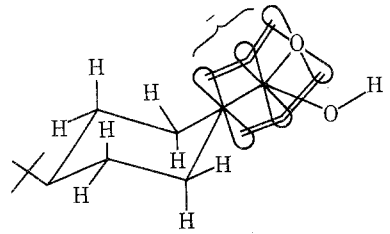


2 3

A modified Birch reduction[4] of 4-*tert*-butylbenzoic acid produced 4-*tert*-butyl-1,5-cyclohexadien-1-oic acid (**4**). Two moles of hydrogen was consumed per mole of **4** using a palladium on carbon catalyst, and a mixture of *cis*- and *trans*-4-*tert*-butylcyclohexanoic acid was produced. Treatment of this mixture with diazomethane, carboxylation,[5] and hydrolysis gave **1**.

The results of base-catalyzed decarboxylation of **1** are given in Table I. The product composition is independent of the per cent yield. The investigation is limited by the fact that **1** was sparingly soluble in aniline and *N*-methylaniline. The diastereomeric product composition is indeed dependent on the choice of basic solvent. If the reasonable assumption is made that the step which controls the stereochemical outcome of decarboxylation of 5,5-dicarboxy-2-isopropyl-1,3-dioxane, *i.e.*, protonation of the enediol intermediate, also obtains in the present study, our results may



be readily explained by comparing the steric hindrance encountered in approach of the conjugate acid of the basic solvent to the upper and lower faces of the intermediate. The syn-axial hydrogens render attack from above more difficult than attack at the lower face. As the bulk of the groups surrounding the acidic site increases, the selectivity increases. The identical product composition (within ex-

perimental error) for pyridine and 2-methylpyridine is possibly due to the fact that the 2-methylpyridinium ion can orient itself in such a manner that the methyl group is positioned away from the syn-axial hydrogens of the ring; such an orientation is not possible for 2,6-dimethylpyridine.

It is of interest that our stereochemical results are comparable to those found in reactions involving approach of a reagent to an exocyclic double bond of a cyclohexane system. Zimmerman and Mariano[6] found that protonation of the enol of 4-phenyl-1-acetylcyclohexane using 2,4,6-trimethylpyridine hydrochloride produced 62 and 78% of the cis isomer in methanol and acetonitrile, respectively. Hydroboration–oxidation[7] and catalytic hydrogenation[8] of 1-methylene-*tert*-butylcyclohexane both produce a preponderance of cis isomer. In each case, the approach is from the less hindered lower face of the molecule.

The lower faces of the cyclohexane and 1,3-dioxane rings are virtually identical.[9] The ratios of the rate of axial attack on the enediol intermediate in the 1,3-dioxane system to that in the cyclohexane system may be readily calculated to be 3.43, 4.22, 2.64, and 18.6 for pyridine, 2-methylpyridine, 2,6-dimethylpyridine, and *N,N*-dimethylaniline, respectively. It is not surprising that the more congested environment of the sp^3 hydridized nitrogen of the *N,N*-dimethylanilinium ion is more selective than the sp^2 hybridized nitrogens in the pyridinium ions.

The anomalously low rate ratio in 2,6-dimethylpyridine shows that an effect in opposition to the steric effect is at work. An attractive possibility is that the transition state in tautomerization of the 1,3-dioxane system is stabilized by coordination of the conjugate acid of the basic solvent to the syn-axial nonbonded electron pairs of the ring oxygens. Since acidity of pyridinium ions decreases as methyl substitution increases, stabilization by coordination becomes less important as the solvent is changed from pyridine to 2-methylpyridine to 2,6-dimethylpyridine.

The fact that 69.7% of **2** is produced in DMF is somewhat surprising. Protonation of the intermediate is undoubtedly by a proton itself, since DMF is too weakly basic for its conjugate acid to be formed in significant concentration. Zimmerman[10] has found that the thermodynamically more stable isomer is the major product when the size of the proton donor decreases. One would expect a larger proportion of the more stable **3** with the tiny proton in DMF, than with the much larger conjugate acids of the basic solvents. One possible explanation is that the effective size of a solvated proton in DMF is quite large. We are currently investigating the effect of the polarity of the solvent on the diastereomeric product composition.

Experimental Section

Gas chromatographic analyses were obtained using a Hewlett-Packard Research Chromatograph, Model 7620A. The nmr spectra were recorded on an Hitachi Perkin-Elmer R-24 nmr spectrometer. Microanalyses were performed by the Baron Consulting Company, Orange, Conn.

4-*tert*-Butylcyclohexane-1,1-dioic Acid. To a dry 2-l. round-bottom three-necked flask, equipped with a mechanical stirrer, a Dry Ice–acetone condenser, and a 100 ml graduated, pressure equalizing addition funnel equipped with a gas inlet adapter was added 51.2 g (287 mmol) of 4-*tert*-butylbenzoic acid and 325 ml of anhydrous diethyl ether. The resulting suspension was stirred while the condenser was filled with Dry Ice–acetone, and the flask was externally cooled with a Dry Ice–acetone bath. Anhydrous ammonia was then admitted to the flask until *ca.* 900 ml of liquid had condensed. The solution was vigorously stirred and 8.6 g of lithium, cut into small pieces each weighing *ca.* 0.3 g, was added over a period of 30 min. After 5 min of stirring, 75 ml of absolute ethanol was cautiously added to the blue solution. When the blue color had disappeared, stirring was stopped, the condenser and cooling bath were removed, and the ammonia and ether were allowed to evaporate. The orange residue was acidified with 1 l. of 6 *M* HCl as the mixture was cooled with an ice–water bath. The precipitate was removed by filtration and dried in a desiccator, yielding 36.9 g (71.0%) of product: pmr (CCl_4) δ 0.90 (s, 9 H), 2.3 (d, J = 3 Hz, 2 H), 5.81 (d, J = 10 Hz, 1 H), 6.38 (d, J = 10 Hz, 1 H), 7.02 (m, 1 H), 11.80 (s, 1 H). The product was tentatively identified as 4-*tert*-butyl-1,5-cyclohexadien-1-oic acid by the method of synthesis[11] and comparison of its pmr spectrum with that of 4-isopropyl-1,5-cyclohexadien-1-oic acid.[4]

A solution of 30.0 g (167 mmol) of product dissolved in 350 ml of diethyl ether was hydrogenated in a Parr apparatus using 0.25 g of 5% palladium on carbon with an initial hydrogen pressure of 60 psi. After the theoretical amount of hydrogen had been taken up, the reaction mixture was filtered through a Celite pad, and concentrated on the rotary evaporator, producing 28.9 g (94.0%) of a white solid, which was shown by treatment with diazomethane and glpc analysis (*vide infra*) to be a mixture of *cis*- and *trans*-4-*tert*-butylcyclohexanoic acid containing a small amount of unreacted 4-*tert*-butylbenzoic acid.

To a 500 ml erlenmeyer flask containing a Teflon coated magnetic stirring bar was added 8 g of KOH dissolved in 15 ml of H_2O. A solution of 40 ml of methanol and 15 ml of diethyl ether was added, and the mixture was chilled to 0°. A solution of 30.0 g (140 mmol) of Diazald (*N*-methyl-*N*-nitroso-*p*-toluenesulfonamide) in 350 ml of diethyl ether is added in small portions, behind a lab shield. After the addition was complete, the mixture was stirred for an additional 10 min, and then cooled to −60°. The solution was decanted and added in small portions to 25.0 g (139 mmol) of the mixture of *cis*- and *trans*-4-*tert*-butylcyclohexanoic acid dissolved in 300 ml of diethyl ether, until the yellow color due to CH_2N_2 persisted. Excess CH_2N_2 was destroyed by the dropwise addition of glacial acetic acid. Most of the solvent was removed on the rotary evaporator, and final concentration was carried out at 50° and 0.5 Torr, producing 26.3 g (95.0%) of an orange oil.

A mixture of the diastereomeric 1-carbomethoxy-4-*tert*-butylcyclohexanoic acids was prepared in 60% yield from the orange oil following the procedure of Reffers, Wynberg, and Strating.[5] Addition of 5.0 g (21 mmol) of the oil to 50 ml of 20% ethanolic KOH produced a mass of white crystals in 10 min. Filtration gave 4.3 g of the crude dipotassium salt, which was dissolved in 20 ml of H_2O, chilled in an ice–water bath, and acidified with 20 ml of 6 *M* HCl. The resulting mixture was saturated with NaCl and filtered to yield 4.1 g (86%) of diacid. Two recrystallizations from benzene gave fine white needles, mp 165–166°.

Anal. Calcd for $C_{12}H_{20}O_4$: C, 63.14; H, 8.83. Found: C, 63.21; H, 8.93.

Decarboxylation Studies. A solution of 50.0 mg of 4-*tert*-butylcyclohexane-1,1-dioic acid, *n*-butyl benzoate (30.0 to 40.0 mg, the internal standard), and 5.00 ml of freshly distilled base was prepared in a dry weighing bottle. Samples of 1.5 ml of this solution were transferred to each of three 5-ml ampoules which had been dried overnight in an oven at 120°. The ampoule was then connected to a vacuum system, plunged into a bath of liquid N_2, evacuated to 0.1 Torr, and sealed. After warming to room temperature, the ampoules were immersed in a silicone oil bath maintained at 100.0° for a period of 24 hr. The ampoules were then plunged into liquid N_2, warmed to room temperature, and opened. Each decarboxylation product was mixed with 5 g of crushed ice in a test tube, and 5 ml of concentrated HCl was added dropwise with swirling. A test with litmus paper established the acidity of the mixture. Extraction with five 2-ml portions of diethyl ether was performed by means of a Pasteur pipet. The combined ether extracts were dried over anhydrous $MgSO_4$ and filtered, and the filtrate was treated with diazomethane as described previously.[2] The mixture of esters was analyzed by glpc (3 ft × 0.25 in., 15% Carbowax 20M on Chromosorb W, 80–100 mesh at 155°, He flow 98 ml/min). The results reported in Table I for each solvent represent the average values of at least 15 glpc analyses. A correction factor for the extraction and analysis was determined using a synthetic mixture of pure *cis*- and *trans*-4-*tert*-butylcyclohexanoic acid. Control experiments demonstrated that epimerization did not occur under the conditions of the decarboxylation.

***cis*-4-*tert*-Butylcyclohexanoic Acid (2).** A mixture of **2** and **3** was treated with CH_2N_2 as described above. The methyl esters were separated by preparative glpc (10 ft × 0.38 in., 25% Carbowax 20M on Chromosorb P, 60–80 mesh, 160°, He flow 55 ml/min). The trans isomer had the longer retention time. To 6 ml of concentrated H_2SO_4 was added 0.673 g (314 mmol) of the pure methyl ester of **2**. After 6 min, the reaction mixture was poured into ice–water,

and extracted with three 25-ml portions of diethyl ether. The combined ethereal extracts were extracted with three portions of 25 ml of saturated $NaHCO_3$. The combined $NaHCO_3$ extracts were acidified at 0° with 6 *M* HCl, and the precipitate (0.154 g) was removed by filtration. The filtrate was saturated with NaCl and extracted twice with 25-ml portions of diethyl ether. Drying the combined ether extracts over anhydrous $MgSO_4$, and concentration on the rotary evaporator, gave an additional 0.037 g of product, making the total yield 0.191 g (30.7%). Recrystallization from benzene gave crystals, mp 117–118° (lit.[11] 117.5–118°).

***trans*-4-*tert*-Butylcyclohexanoic Acid (3).** Hydrolysis of 0.565 g (2.85 mmol) of the pure methyl ester of **3** by the procedure described for the methyl ester of **2** gave 0.202 g (35.4%) of **3**, mp 173–174° (lit.[11] 174–175°).

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Registry No.—**1**, 53783-19-0; **2**, 943-28-2; **3**, 943-29-3; 4-*tert*-butylbenzoic acid, 98-73-7; 4-*tert*-butyl-1,5-cyclohexadien-1-oic acid, 31673-51-5; *cis*-1-carbomethoxy-4-*tert*-butylcyclohexanoic acid, 53783-20-3; *trans*-1-carbomethoxy-4-*tert*-butylcyclohexanoic acid, 53783-21-4.

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1,6-Methano[10]annulene *via* a Solvolytic Pathway

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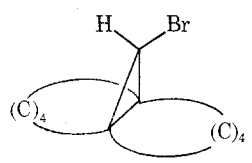
We and others have recently reported on the chemistry of various tricyclic dihalocyclopropanes.[1–8] Continued interest in this area has led us to study monohalo tricyclic systems of the general type **1**. We now wish to report on the chemistry of 11-bromotricyclo[4.4.1.$0^{1,6}$]undeca-3,8-diene (**2**). When **2** is treated with methanolic silver nitrate at



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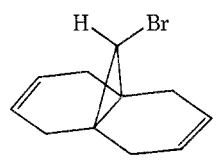

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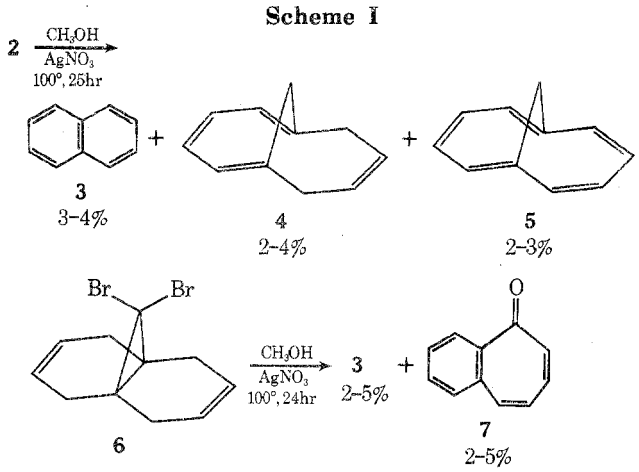
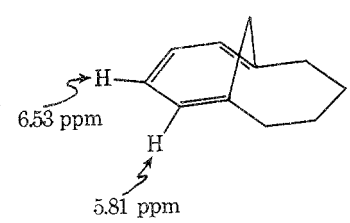
100°, three volatile products are obtained in a combined absolute yield of approximately 10% (Scheme I). The remaining, nonvolatile reaction product consists of apparently polymeric, intractable material from which we have not been able to isolate characterizable material by the usual separation techniques.

Scheme I



Compound **3** was readily identified as naphthalene by comparison of its nmr and infrared spectra with authentic material. The nmr spectrum of **5** was identical in all respects with that of the 1,6-methano[10]annulene published by Vogel.[9]

The structure of the tetraene **4** was assigned based on spectral data.[10a] The nmr of **4** exhibits absorption at 0.68 ppm (J = 9 Hz, 1 proton), 2.63 ppm (J = 9 Hz, 1 proton), 2.75–3.15 ppm (complex absorption, 4 protons), 5.32 ppm (broad singlet, 2 protons), 5.77 ppm (broad singlet, 2 protons), and 6.62 ppm (doublet of doublets, 2 protons). The low-field absorptions at 5.77 and 6.62 ppm are virtually identical in line shape and nearly identical in field position with the low-field absorptions reported by Vogel for the triene **8**.[10b,11]



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While the volatile products obtained from **2** are quite different from those obtained from **6**, the rates of silver ion assisted solvolysis are similar (Table I).

If one assumes that the rate-determining step in the solvolysis of each compound is the formation of a cyclopropyl cation, then any difference in rate between the two compounds should be a reflection of the difference in ground-state energy between the two. Implicit in this argument is the assumption that the cyclopropyl cation is planar and the further assumption that the effect of the α-bromo sub-

Table I[a]
Rate Constants and Activation Parameters of the Ag^+-Assisted Solvolysis of 2 and 6

Compd	Temp,[c] °C	k, l. mol^{-1} sec^{-1}	k_{rel} (25°)	ΔH^*, kcal/mol	ΔS^*, eu
	140	1.89×10^{-3} (±0.02)			
2	124	5.03×10^{-4} (±0.06)	1	27.6	−4.7
	25	3.12×10^{-9} [b]			
6[8]	25	6.97×10^{-9} [b]	2.2	30.3	5.7

[a] Silver perchlorate (~20-fold excess) in 95% methanol was employed in all solvolyses. [b] This is an extrapolated value. [c] At least two runs were made at each temperature.