erately intense band at 1555 cm^{-1}. No other carbonyl bands were observed nor was there any absorption between the carbon–hydrogen stretching region and 1750 cm^{-1}.

2-Diphenylhydroxymethyl-1,1,5,5-tetraphenyl-3-pentanone (9).—A 15.4% yield of this compound was isolated, following the procedure of Kohler and Heritage,[11,14] mp (fast) 154–155°, lit.[11] 153°. The infrared spectrum is compatible with the assigned structure. Refluxing with 10% sodium hydroxide solution for 2 hr followed by ether extraction afforded 1,1,5,5-tetraphenylpentanone-3, mp 125.5–127.0° (lit.[14] 130°). On heating in a *kugelrohr* at 30° (11 mm) two pure products condensed on the cooler parts of the tube: the white solid was the above pentanone, and the liquid proved to be benzophenone by tlc (silica gel–benzene) comparison with authentic samples.

Attempts to prepare **9** from reagent **5** by addition of phenylmagnesium bromide solution were fruitless, only **7a** being isolated in 41.5% yield (crude). A considerable variety of unidentified products was obtained by chromatographic procedures and each, which could be isolated relatively pure (tlc), was checked by tlc for identity with **9** and its two decomposition products, none of which was detected.

Kohler's 7a.—The crude product had mp 200.5–206.5° and was recrystallized from ethanol–chloroform to give satin-white needles [dried over phosphorus pentoxide at 80° (5 mm)], mp 209.2–210.7°. A second recrystallization with 3 days of drying as before gave mp 216.0–217.5° (lit.[14] 211–213°); ir (KBr) 1760 1720, and 1665 cm^{-1}; nmr chemical shifts nearly identical with those for authentic **7a**. The integrated nmr peaks fit methyl 2,4-dibenzhydryl-3,5-dioxo-7,7-diphenylheptanoate: mass spectrum (70 eV) *m/e* 656 (parent ion); isotopic abundance ratios at *m/e* 656 (Calcd: 100, 51.65, 14.10. Found: 100, 51.5, 14.3.); conventional mol wt (vapor pressure[1] in chloroform) 680.

Registry No.—Methyl 2-bromo-3,3-diphenylpropanoate, 24689-50-7; dimethyl 2,3-dibenzhydrylsuccinate, 24728-01-6; **6**, 24689-51-8; **7a**, 24647-01-6.

Enthalpy, Entropy, and Free-Energy Changes in the Equilibration of *cis*- and *trans*-Ethyl 3-*t*-Butylcyclobutanecarboxylate and 3-*t*-Butylcyclobutanol

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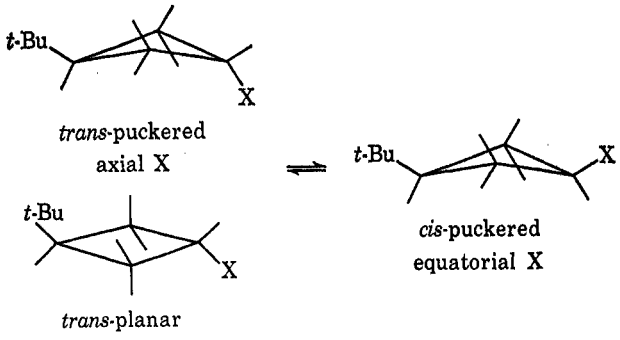
The *cis*- and *trans*-3-*t*-butylcyclobutanols have been prepared and equilibrated with aluminum isopropoxide in isopropyl alcohol at different temperatures. The thermodynamic parameters (*trans* to *cis*) are $\Delta H = -1.6$ kcal/mol, $\Delta S = -1.1$ cal/(deg mol), and $\Delta G_{100} = -1.15$ kcal/mol. The equilibration of ethyl 3-*t*-butylcyclobutanecarboxylate with sodium ethoxide in ethanol at different temperatures gives $\Delta H = -0.8$ kcal/mol, $\Delta S = -0.7$ cal/(deg mol), and $\Delta G_{100} = -0.58$ kcal/mol. The *cis* isomers are enthalpically favored while the *trans* isomers are entropically favored. The results have been explained on the basis of a relatively rigid puckered *cis* isomer and a somewhat flexible *trans* isomer.

The free-energy change in the equilibration of ethyl *cis*- and *trans*-3-*t*-butylcyclobutanecarboxylate has been previously reported.[1] The *cis* isomer predominates at equilibrium in support of the idea that the ring is puckered leading to the groups being placed in equatorial positions similar to those in cyclohexane (Chart I, X = CO_2Et). The *trans* isomer, on the other hand, would have an equatorial *t*-butyl and an axial carbethoxyl group provided that the ring is puckered to the same extent as in the *cis* isomer (Chart I, X = CO_2Et). The argument commonly used in conformational studies in cyclohexane would indicate that the enthalpy of the *trans* isomer would be higher than that of the *cis* one due to a 1,3 interaction. However, it is possible that this interaction may be great enough to result in a planar ring (Chart I, X = CO_2Et). Either way, the *trans* isomer should have the higher enthalpy since the puckered form would have a greater 1,3 interaction, increased angle strain, and better torsional angles, while the planar form would have a reduced 1,3 interaction, decreased angle strain, and poorer torsional angles. The actual structure for the *trans* isomer may be somewhere between the extremes.[1]

Experimental evidence supports conformations of rings varying between significantly puckered to planar ones for substituted cyclobutanes. For example, the *cis* isomers of methyl 3-methylcyclobutanecarboxylate,[2]

CHART I

EQUILIBRATION OF PLANAR AND NONPLANAR 3-*t*-BUTYLCYCLOBUTYL DERIVATIVES



X = CO_2Et, OH

3-isopropylcyclobutyl alcohols and amines,[3] methyl 3-isopropylcyclobutanecarboxylate,[4] 2,2,4,4-tetramethylcyclobutane-1,3-dinitrile,[5] 1,3-dibromocyclobutane,[6] and 1,3-cyclobutanedicarboxylic acid[7] all have been shown to be puckered, and calculations on 1,3-dimethylcyclobutane indicate that this should be expected.[8] On the other hand, conformations of the

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trans isomers of the above compounds vary from planar or nearly planar for methyl 3-isopropylcylcobutanecarboxylate[4,9] and 1,3-cyclobutanedicarboxylic acid[10] to significantly puckered 2,2,4,4-tetramethylcyclobutane-1,3-dinitrile[5] and 1,3-dibromocyclobutane.[6] Solid-state forces play an important role in determining the structure of *trans*-1,3-cyclobutanedicarboxylic acid since when alone in the crystal the ring is planar,[10] while the diacid is puckered in the sodium salt, $Na_2C_4H_6(CO_2^-)_2 \cdot 2C_4H_6(CO_2H)_2$.[11] Thus, it is not known whether the diacid would be puckered or planar in solution.

In this paper, the ethyl *cis*- and *trans*-3-*t*-butylcyclobutanecarboxylates synthesized previously[1] have been equilibrated at different temperatures in order to obtain ΔH and ΔS. In addition, the synthesis and equilibration of the *cis*- and *trans*-3-*t*-butylcyclobutanols (Chart I, X = OH) at different temperatures is reported. An independent report of the synthesis of the alcohol appeared while this work was in progress,[12] but no equilibrium studies were made. A comparison of the thermodynamic parameters for the two equilibrations would be of interest in order to help clarify the conformation situation indicated in Chart I. Although the conformational situation in cyclobutane is not completely analogous to cyclohexane, there are some similarities, and the enthalpies and entropies of the carbethoxyl[13] and hydroxyl[14] groups in cyclohexane have recently been reported.

The 3-*t*-butylcyclobutanols were synthesized starting from a mixture of *cis*- and *trans*-3-*t*-butylcyclobutanecarboxylic acids (**1**).[1] The acid **1** was converted to the acid chloride **2** and then to methyl 3-*t*-butylcyclobutyl ketone (**3**) with dimethylcadmium. The ketone **3** was converted to 3-*t*-butylcyclobutyl acetate (**4**) with perbenzoic acid. The acetate **4** was hydrolyzed to give 3-*t*-butylcyclobutanol (**5**) which was separated into the *cis* and *trans* isomers.[15] Peak one, the largest component in a chromatogram of the alcohols, corresponded to the *cis* isomer as was found with the esters.[1] The *cis* acid **1** predominated in the starting material and by about the same amount found in the alcohols. The nuclear magnetic resonance (nmr) spectra of the alcohols are consistent with the generalization found in cyclohexane[16,17] that an equatorial proton is less shielded than the corresponding axial one. The axial proton next to hydroxyl appears at τ 6.0 in the *cis* isomer while the resonance for the equatorial proton is at τ 5.7 in the *trans* isomer. A similar relationship was observed in the ethyl 3-*t*-butylcyclobutanecarboxylates[1] and in the 3-isopropylcyclobutanols.[3] While the *trans* alcohol is probably not so puckered as the *cis* alcohol, the qualitative argument would probably still hold.

The alcohol **5** was oxidized to 3-*t*-butylcyclobutanone (**6**) by means of ruthenium tetroxide. Lithium aluminum hydride reduction of the ketone **6** gave a mixture composed of 91% *cis* alcohol **5**. If one assumes a planar ring as in the case of cyclobutanone itself,[18] it seems reasonable that steric approach control may operate to give predominately the *cis* isomer.

The ethyl *cis*- and *trans*-3-*t*-butylcyclobutanecarboxylates were equilibrated at five different temperatures from 80 to 151° with sodium ethoxide in absolute alcohol in sealed ampoules. Each isomer and a mixture were equilibrated at 80 and 151° and only a mixture for the other temperatures. Previously, the time found adequate for complete equilibration was 450 hr[1] at 80°, and as seen in Table I this has been exceeded by more than a factor of 2. In addition, tubes were removed from the bath at two different times. The equilibrium constants, recorded in Table I, are the averages obtained from 9 to 18 chromatograms and indicate that the *cis* isomer predominates at all temperatures.

TABLE I

EQUILIBRIUM CONSTANTS AS A FUNCTION OF TEMPERATURE

Compound	Temp, °C	Time, hr	K = *cis*/*trans*
Ethyl 3-*t*-butylcyclobutanecarboxylate (X = CO_2Et in Chart I)	80.1 ± 0.1	1052, 1269	2.33 ± 0.11
	100.0 ± 0.1	1139, 1218	2.19 ± 0.05
	110.3 ± 0.5	1139, 1288	2.12 ± 0.02
	134.8 ± 0.9	1139, 1288	1.97 ± 0.05
	150.8 ± 0.7	1139	1.92 ± 0.04
3-*t*-Butylcyclobutanol (X = OH in Chart I)	100.1 ± 0.3	165, 207, 355	4.77 ± 0.07
	137.4 ± 0.3	184, 208	3.91 ± 0.07
	154.2 ± 1.2	138, 184, 208	3.64 ± 0.07

The equilibrium constants for 3-*t*-butylcyclobutanol shown in Table I were obtained at the temperatures indicated by reaction of 3-*t*-butylcyclobutanone with aluminum isopropoxide in isopropyl alcohol. The ketone was shown by gas chromatography to reduce rather quickly, followed by the equilibration of the resulting alcohols. As a check, mixtures rich in the *cis* and *trans* alcohols were each equilibrated at 100 and 154°, and the same equilibrium constants were found as those given in the table (well within experimental error). Tubes were removed from the bath at two or three different times in order to ensure that equilibrium had been attained. Seven to ten chromatograms were analyzed to obtain the constants given in Table I. Again, the *cis* isomer predominates at all temperatures as with the esters. Raney nickel[19,20] has been used for equilibrating alcohols in the cyclohexane series. Although the method is somewhat more convenient, particularly in solvents other than alcohol,[20] the cyclobutane ring may undergo cleavage at higher temperatures. Thus, the method was not employed. In any case, the aluminum isopropoxide and Raney nickel methods give similar results for the conformational free energy of the hydroxyl group in the cyclohexane ring.[20] Since the presence of aluminum alkoxide does not change the position of the equilibrium, presumably both methods involve the free alcohol, or

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TABLE II

THERMODYNAMIC PARAMETERS FOR EQUILIBRATION OF CYCLOBUTYL AND CYCLOHEXYL ESTERS AND ALCOHOLS

Compound	ΔH, kcal/mol	ΔS, cal/(deg mol)	ΔG_{100}, kcal/mol
Ethyl 3-*t*-butylcyclobutanecarboxylate (*trans* → *cis*; axial → equatorial in Chart I)	−0.8 ± 0.2	−0.7 ± 0.5	−0.58 ± 0.02
3-*t*-Butylcyclobutanol (*trans* → *cis*; axial → equatorial in Chart I)	−1.6 ± 0.2	−1.1 ± 0.5	−1.15 ± 0.01
Ethyl 4-*t*-butylcyclohexanecarboxylate (axial → equatorial)	−1.09[a]	+0.4[a]	
4-*t*-Butylcyclohexanol (axial → equatorial)	−1.09[b]	−0.46[b]	

[a] Reference 13. [b] Reference 14.

nearly so, at least in the cyclohexane ring. This may also be the situation in the present work.

Log K was plotted against $1/T$ resulting in excellent visual fits to straight lines in both cases. From the slopes of the lines, the enthalpies were obtained (slope $= -\Delta H/2.3R$), and this together with the equations $\Delta G = \Delta H - T\Delta S$ and $\Delta G = -RT \ln K$ gave the entropies and free energies. The thermodynamic parameters obtained for the cyclobutyl esters and alcohols are shown in Table II together with comparison data for the corresponding cyclohexanes. The error limits for the cyclobutyl compounds given in Table II were calculated in the following manner.[13] The equilibrium constants at the higher temperatures were increased and the ones at the lower temperatures decreased by the amounts of the standard deviations given in Table I. After a line was drawn through the new points, ΔH was recalculated. The procedure was repeated so that the constants at the higher temperatures were now lowered, the values at the lower temperatures were increased by the standard deviations, and the value of ΔH was calculated. The new values of ΔH were used to set the error limits. Thus, it is felt that the values given represent the extreme confidence limits of the thermodynamic parameters calculated in this study.

As expected, the enthalpies in each of the equilbrations of the cyclobutyl compounds were negative in keeping with the explanation given above and the situation in Chart I where the *cis* isomer is favored enthalpically. Before discussing the difference in magnitude between the enthalpies of the alcohols and esters, note should be made of the signs and magnitude of the entropy values. In both cases the *trans* isomers are favored entropically. This result might be expected in the case of the alcohols since it has been shown that the more accessible equatorial hydroxyl in a cyclohexane ring is solvated more strongly than the hindered axial group.[14] Using this analogy, it seems reasonable that the hydroxyl in the *cis* cyclobutyl alcohol would be more strongly solvated (lower entropy) than the *trans* alcohol (higher entropy) in either of the extreme puckered or planar conformations in Chart I. Therefore, a negative entropy change (*trans* → *cis*) is observed as is found in the cyclohexane ring (a → e) as given in Table II.

In explaining the negative entropy change for the esters, it would again be of interest to look at data given in Table II for the carbethoxyl group in the cyclohexane ring. The isomer with the equatorial carbethoxyl[13,21,22] and carbomethoxyl[23,24] group has the higher entropy in both the 3- and 4-*t*-butylcyclohexanecarboxylates. This result, inconsistent with a solvation argument, is explained on the basis of the axial group being subjected to greater rotational restrictions (lower entropy) than the equatorial group which can occupy a larger number of populated rotational conformations (higher entropy). The entropy change (a → e) recorded in Table II for carbethoxyl is therefore found to be positive in contrast to compounds with groups such as hydroxyl[14] and carboxyl[13] where the change (a → e) is negative.

It seems unlikely that the negative entropy change observed in the cyclobutyl esters would be caused by a solvation effect as apparently this is unimportant for esters in the cyclohexane ring.[13] Thus, it may appear that the carbethoxyl group in the *trans* isomer actually has more rotational freedom (higher entropy) than one would predict on the basis of the cyclohexane analogy, in comparison with the *cis* isomer (lower entropy). Perhaps, one of the methyls on the *t*-butyl group extends over the ring to some extent and thereby restricts the rotation of the carbethoxyl group in the *cis* isomer relative to the situation in the *trans* one. However, any large measure of interaction of the *t*-butyl group with the functional group would tend to increase the enthalpy of the *cis* isomer and reduce its concentration at equilibrium.

The most reasonable explanation might be in the flexibility of the cyclobutane ring itself. It is known that the difference in energy between a puckered and planar cyclobutane ring[25] is small. Thus, at the temperatures used in the equilibrations, the *trans* isomer might be undergoing continuous conformational change (higher entropy) leading to a number of conformers with nearly equal energies. On the other hand, the *cis* isomer might be expected to be more rigid (lower entropy) since moving toward a planar ring would create an increased interaction between the *t*-butyl and carbethoxyl, and more puckering would increase angle strain. Part of the entropy change observed with the alcohols could also be due to greater flexibility of the *trans* isomer as compared with the *cis* one, although

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solvation effects are probably more important as discussed previously.

Returning to the difference in magnitude of the enthalpy changes in the alcohols and esters, it is seen in Table II that the *cis* cyclobutyl alcohol is favored enthalpically ($\Delta H = -1.6$) to a greater extent than the *cis* ester ($\Delta H = -0.8$). In the cyclohexane ring, a large solvent effect on the enthalpy change has been observed for the hydroxyl group probably because of the added stability given to the equatorial isomer due to hydrogen bonding.[14,20] For example, ΔH can vary from -0.62 to -1.09 as the solvent is changed from cyclohexane to isopropyl alcohol, the latter value being essentially the same as that found for the carbethoxyl group[13,21,22] (Table II). It is possible that a much greater solvent effect is being observed in the present case than seen in the cyclohexane ring. However, it appears somewhat more likely that the larger carbethoxyl group may be closer to the *t*-butyl group than the hydroxyl in the *cis* isomers. Thus, the effect might be to decrease the enthalpy difference between the *cis* and *trans* esters below that of the alcohols.

It seems reasonable to assume that the thermodynamic parameters ΔH, ΔS, and ΔG, for other 3-*t*-butylcyclobutyl derivatives (*trans* → *cis*) may also be negative. Thus, it would be of interest to investigate other groups such as the carboxyl and acetyl and to investigate hydroxyl in other solvents.

Experimental Section

3-*t*-Butylcyclobutanecarbonyl Chloride (2).—A mixture of 15.0 g (0.096 mol) of 3-*t*-butylcyclobutanecarboxylic acid[1] (1) and 21.2 g (0.179 mol) of freshly distilled thionyl chloride was allowed to stand at room temperature for 0.5 hr and then was heated at reflux for an additional 1.5 hr. The excess thionyl chloride was removed under reduced pressure, and the residue was distilled to give 16.0 g (96%) of *cis*- and *trans*-3-butylcyclobutanecarbonyl chloride, bp 86–87° (15 mm).

Methyl 3-*t*-Butylcyclobutyl Ketone (3).—A 250-ml three-necked flask containing 60 ml of anhydrous ether was fitted with an inlet tube dipping below the surface of the ether and an outlet protected with a drying tube. The ether was cooled in an ice–salt bath and weighed, and methyl bromide from a gas cylinder was added through the inlet tube until the gain in weight was 11.4 g (0.12 mol). Into a 1-l. three-necked flask, equipped with a stirrer, reflux condenser, and an addition funnel with a tube extending to the bottom of the flask, were placed 2.8 g (0.115 g-atom) of magnesium turnings, 40 ml of anhydrous ether, and a crystal of iodine. The cold solution of methyl bromide was transferred to the addition funnel and added with stirring over a 25-min period during which time the mixture refluxed spontaneously. The magnesium had completely reacted after a total of 30 min.[26] The flask was then cooled, and 11.3 g (0.061 mol) of cadmium chloride (dried to constant weight at 110°) was added over a period of 7 min. The ice bath was removed and the mixture was stirred for 15 min and then heated under reflux with stirring for an additional hour. Ether (50 ml) was distilled until a viscous residue remained. Dry benzene (80 ml) was added and the distillation continued until an additional 50 ml of distillate was obtained. Dry benzene (100 ml) was again added and the mixture refluxed with stirring for 15 min. The heating bath was removed and 16.0 g (0.092 mol) of **2** dissolved in 30 ml of dry benzene was added dropwise over a 5-min period with stirring. After the addition of the acid chloride was completed and spontaneous refluxing had stopped, the mixture was stirred and heated under reflux for an additional hr. To the cooled mixture was added 100 ml of ice water followed by sufficient 20% sulfuric acid to give two phases. The aqueous phase was separated and extracted with 25 ml of benzene. The combined organic layers were washed successively with 40 ml of water, 40 ml of dilute sodium bicarbonate, and 20 ml of saturated salt solution. The benzene was flask distilled after drying over anhydrous sodium sulfate.[27] The residue was distilled to give 9.2 g (65% based on the acid chloride) of *cis*- and *trans*-methyl 3-*t*-butylcyclobutyl ketone: bp 85–87° (16 mm); nmr (CCl_4) τ 7.1 (m, 1, CHCO), 7.94 and 7.98 (s, 3, $COCH_3$), 8.08 (m, 5, ring), 9.15 and 9.20 [s, 9, $C(CH_3)_3$]. Analysis by gas chromatography (12-ft 35% diethylene glycol succinate on 45–60 Chromosorb W column at 100° at 30 psi) gave retention times of 28 and 31 min for the *cis* and *trans* isomers, respectively. The order of elution and the composition was the same as previously found.[1] *Anal.* Calcd for $C_{10}H_{18}O$: C, 77.9; H, 11.8. Found: C, 77.9; H, 12.0.

3-*t*-Butylcyclobutyl Acetate (4).—To 290 ml of 0.38 *M* perbenzoic acid (15.2 g, 0.11 mol) in chloroform[28] contained in a 500-ml flask was added 9.2 g (0.060 mol) of **3**. The flask was wrapped to exclude light and allowed to stand at room temperature for 48 hr. At this time, 0.063 mol of perbenzoic acid had been consumed as determined iodimetrically.[28] The remaining perbenzoic acid was decomposed with an excess of sodium iodide dissolved in water, followed by addition of a solution of sodium thiosulfate until colorless. The chloroform layer was then extracted with aqueous sodium carbonate to remove benzoic acid and dried over magnesium sulfate, and the chloroform was distilled.[29] The residue was distilled to give 7.2 g (71%) of *cis*- and *trans*-3-*t*-butylcyclobutyl acetate: bp 101–105° (30 mm); nmr (CCl_4) τ 5.1 (m, 1, CHOAc), 7.8 and 8.3 (m, 5, ring), 8.00 and 8.03 (s, 3, $COCH_3$), 9.13 and 9.17 [s, 9, $C(CH_3)_3$]. Analysis by gas chromatography under the conditions above gave retention times of 25 and 27 min for the *cis* and *trans* isomers, respectively. The composition was about the same as the original ketone mixture. *Anal.* Calcd for $C_{10}H_{18}O_2$: C, 70.6; H, 10.7. Found: C, 70.6; H, 10.8.

3-*t*-Butylcyclobutanol (5).—To 3.2 g (0.057 mol) of potassium hydroxide dissolved in 29 ml of methanol was added 7.2 g (0.0424 mol) of **4**. The resulting solution was heated under reflux for 3 hr. The cooled solution was diluted with 60 ml of water and extracted four times with 30-ml portions of ether. The combined extracts were dried over magnesium sulfate and the ether was removed by distillation. The residue was distilled to give 4.05 g (75%) of *cis*- and *trans*-3-*t*-butylcyclobutanol, bp 99–100° (19 mm). A sample was purified by gas chromatography. *Anal.* Calcd for $C_8H_{16}O$: C, 74.9; H, 12.6. Found: C, 74.6; H, 12.5. The product was analyzed by gas chromatography and indicated a composition of 70% *cis* and 30% *trans*. The retention times on a 20-ft 30% SE-30 on 45–60 Chromosorb W column at 100° at 200 ml/min were 33 and 37 min and on a 11-ft 30% dioctyl phthalate on 45–60 Chromosorb W column at 130° at 30 psi were 39 and 42 min for the *cis* and *trans* isomers, respectively: nmr *cis* (CCl_4) τ 6.0 (m, 1, CHOH), 5.9 (s, 1, OH), 7.88 (m, 2, CH_2), 8.40 (m, 3, CH_2, CH), 9.17 (s, 9, $C(CH_3)_3$); *trans* (CCl_4) τ 5.7 (m, 1, CHOH), 6.2 (s, 1, OH), 7.90 (m, 5, ring), 9.15 [s, 9, $C(CH_3)_3$].

3-*t*-Butylcyclobutanone (6).—Sodium periodate (4.2 g, 0.020 mol) and 0.011 g of ruthenium trichloride hydrate were dissolved in 30 ml of water and added to 1.32 g (0.0103 mol) of **5** in 5 ml of carbon tetrachloride. The resulting mixture was stirred vigorously with a magnetic stirrer for 24 hr.[30] The layers were separated, and the aqueous layer was extracted with two 15-ml portions of chloroform. The combined organic layers were dried over magnesium sulfate, and the solvent was removed by distillation. The residue was distilled to give 0.90 g (68%) of 3-*t*-butylcyclobutanone: bp 85° (20 mm); nmr (CCl_4) τ 7.2 (m, 4, CH_2), 7.7 (m, 1, CH), and 9.06 [s, 9, $C(CH_3)_3$]. Analysis by gas chromatography on the above columns indicated one component. The ir spectrum showed the typical cyclobutanone carbonyl stretch at 5.6 μ. *Anal.* Calcd for $C_8H_{14}O$: C, 76.1; H, 11.2. Found: C, 76.2; H, 11.1.

Reduction of 3-*t*-Butylcyclobutanone with Lithium Aluminum Hydride.—To 0.187 g (4.92 mmol) of lithium aluminum hydride dissolved in 4 ml of anhydrous ether in a 50-ml flask was added 0.45 g (3.60 mmol) of **6** dissolved in 4 ml of ether over a 10-min period, with magnetic stirring. The mixture was then allowed to reflux for 30 min. To the cooled mixture was added 3.5 ml of 30 wt % aqueous potassium sodium tartrate until the gray solid was replaced by a white solid and an aqueous layer. The layers

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(28) G. Braun, ref 26, Coll. Vol. I, 1941, p 431.

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were separated, and the aqueous layer was extracted twice with 4-ml portions of ether. The combined extracts were dried over magnesium sulfate, and the ether was distilled to give 0.38 g (85%) of 3-*t*-butylcyclobutanol as a residue that was not further purified. This residue was analyzed by gas chromatography on the 20-ft SE-30 column which indicated a composition of 91% *cis* and 9% *trans*. No other components were observed.

Equilibration of 3-*t*-Butylcyclobutanol.—A 0.6 *M* solution of aluminum isopropoxide in isopropyl alcohol was prepared by refluxing 3.28 g of aluminum and 0.16 g of mercuric chloride in 200 ml of isopropyl alcohol (reagent grade, heated at reflux over calcium oxide for 7 hr) for 8 hr.[31] There was a small amount of black precipitate formed that was removed by centrifuging and decanting the clear solution. Enough solution for 5 ampoules was obtained by dissolving 0.125 g of 3-*t*-butylcyclobutanone (**6**) in 1.65 ml of the above solution, yielding a solution approximately 0.6 *M* in each reactant. The solutions were distributed into test tubes, flushed with dry nitrogen, sealed, and immersed in baths at the temperatures indicated in Table I. The baths consisted of various liquids in flasks which were brought to reflux and maintained at their boiling points. The temperatures were found to remain constant within the limits given in Table I and were corrected with a National Bureau of Standards thermometer. The ampoules were removed at the times indicated in Table I, cooled in ice water, and opened immediately. To the contents was added 1 ml of 6 *N* HCl, and this solution was then extracted with two 1-ml portions of ether. After removal of the ether, the residue was analyzed by gas chromatography on the 20-ft 30% SE-30 column used above for separation of the alcohols. The equilibrium constants were calculated from the ratio of the peak areas obtained by the height times half band width method. Each value in Table I is the average of seven to ten chromatograms from at least two different tubes. Analysis of a mixture of known composition indicated that repsonse corrections were unnecessary.

As a check on the use of the ketone **6** for obtaining the equilibrium constants, mixtures rich in the *cis* and *trans* alcohols **5** were each equilibrated separately. A solution of 0.125 g of 3-*t*-butylcyclobutanol, rich in either the *cis* or *trans* isomer, 0.31 g of ketone **6**, and 1.65 ml of 0.6 *M* aluminum isopropoxide–isopropyl alcohol was prepared and equilibrated as above. At 100°, the initial *cis* and *trans* rich mixtures gave equilibrium constants of 4.83 ± 0.14 and 4.75 ± 0.13, respectively. At 154°, the initial *trans* rich mixture gave an equilibrium constant of 3.62 ± 0.07.

Equilibration of Ethyl 3-*t*-Butylcyclobutanecarboxylate.—The procedure used to equilibrate the esters was described previously.[1] Sealed ampoules were immersed in the baths described above at the temperatures indicated in Table I and removed at the times given. The ampoules were cooled in ice water, opened, and worked up as before.[1] The concentrate was analyzed by gas chromatography on the 20-ft 30% column used above. The retention times on this column at 130° and 200-ml/min pressure were 51 and 56 min for the *cis* and *trans* esters, respectively. The equilibrium constants were obtained by the method above, and the averages of from 9 to 18 chromatograms are given in Table I. A 50:50 mixture was used to obtain the constants at 100, 110, and 135°. As a check on the use of this mixture, pure *cis* and *trans* isomers were each independently equilibrated at 80 and 151°. The equilibrium values thus obtained from both sides were identical and have been included in the averages in Table I. Tubes were removed at several times and the compositions were found to be identical. No correction factor was necessary for calculation of the equilibrium constants, as shown by gas chromatogaphic analysis of a known mixture prepared from weighed samples of the pure esters.

Registry No.—*cis*-**1** ethyl ester, 14924-51-7; *trans*-**1** ethyl ester, 14924-52-8; *cis*-**2**, 24165-52-4; *trans*-**2**, 24165-53-5; *cis*-**3**, 24122-09-6; *trans*-**3**, 24122-10-9; *cis*-**4**, 24122-12-1; *trans*-**4**, 24122-13-2; *cis*-**5**, 20588-76-5; *trans*-**5**, 20476-25-9; **6**, 20614-90-8.

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Studies of Benzonorbornene and Derivatives. IV.[1] Bridgehead and 1-Carbinyl Derivatives[2,3]

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Benzonorbornenyl-1-carbinyl tosylate (**1**) is investigated as a possible model for a non-π-participatory neophyl system. Its solvolysis compared with that of the nonbenzo analog **9** is retarded 47-fold in acetic acid at 133° and 14-fold in 80% acetone at 25°. No evidence for anchimeric assistance by the aromatic ring was found. Under the vigorous conditions of refluxing hydrobromic acid containing zinc bromide, benzonorbornenyl-1-carbinol (**8**) still failed to allow aromatic migration, although both methano and ethano bridge-migrated products were detected. Benzonorbornenyl-1-carbinyl radical, produced by radical-promoted decarbonylation of the aldehyde **22**, did not rearrange. The absence of rearrangement illustrates the necessity of twist in the aromatic ring during rearrangement. From benzonorbornene-1-carboxylic acid (**2**) synthetic prodedures to a number of the title compounds are described.

Recently our interest in benzonorbornene chemistry coincided with other interests in homoallylic π-electron systems[4] and ring-size effects in the neophyl rearrangements.[5] All three of these interests led to the present investigation of benzonorbornenyl-1-carbinyl derivatives. Incidental to this work was the synthesis of a number of heretofore unknown bridgehead-substituted benzonorbornenes.[6]

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