15), 3.19 (broadened s, 2), 6.60 (m, 1); ir (CS_2) 1395 (m), 905 (m), 828 cm^{-1} (m); ir ($CHCl_3$) 2950 (s), 1620 (m, C=C stretching), 1451 cm^{-1} (s); uv max (95% EtOH) 220 nm (ϵ 20,900), 225 (21,700).

Anal. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C, 90.15; H, 9.82.

Isolated and synthetic samples (*vide infra*) of **5** were identical.

Syntheses of Reference Compounds. 2,4,5,6,7-Pentamethyl-1-indanone (11).[10] A mixture of 11.5 g (0.086 mol) of 1,2,3,4-tetramethylbenzene, 15 g (0.083 mol) of methyl 3-bromoisobutyrate,[11] and 50 g of anhydrous $AlCl_3$ was maintained at 135° until evolution of hydrogen halide gas ceased (2 hr). The reaction mixture was treated with ice-water and extracted with benzene. Evaporation of the extract left a solid which was recrystallized from MeOH and then stirred and heated (steam bath) with 125 ml of concentrated H_2SO_4 for 14 hr. The mixture was poured into ice-water and extracted with benzene. Evaporation gave a crude solid which was purified by repetitive evaporative distillation at 130° (0.5 mm) to give 3.7 g (22%) of **11**, mp 72-76°, converted to needles (mp 85-86°) on recrystallization from MeOH: pmr ($CDCl_3$) δ 1.31 (d, 3, J = 7.3 Hz, CH_3 at C-2), 2.64 (s, 3, CH_3 at C-7) superimposed on 1.8-3.5 (m, 12, H-2, 2 H-3, 3 CH_3);[12] ir (CS_2) 2980, 2950, 1705 (C=O),[13] 1328, 1282, 1148 cm^{-1}; ir ($CHCl_3$) 1587, 1462, 1385 cm^{-1}.

Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.99; H, 9.04.

2,4,5,6,7-Pentamethyl-1-indanol (12). To a stirred, cold (0°) suspension of 0.5 g of $LiAlH_4$ in 90 ml of ether was added dropwise a solution of 2 g of **11** in 10 ml of ether. After further stirring (2 hr), the cold mixture was treated with aqueous NH_4Cl and extracted with ether. Evaporation of solvent and recrystallization of the residue from MeOH gave 0.7 g (35%) of **12** as white prisms: mp 130-131°; pmr (CCl_4) δ 1.02 (d, 3, J = 7 Hz, CH_3 at C-2), 1.5-3.4 (m, 16, H-1, H-2, 2 H-3, 4 CH_3),[14] 4.6 (broad signal, 1, OH); ir (CS_2) 2970, 2940 cm^{-1}; ir ($CHCl_3$) 3625 (OH), 1464, 1387 cm^{-1}.

Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.03; H, 9.58.

2,4,5,6,7-Pentamethylindene (5). An intimate mixture of 0.3 g of carbinol **12** and 3 g of alumina was heated at 150° (1 atm) for 2 hr and then evaporatively distilled (150°, 0.6 mm) to give 0.14 g (51%) of crystalline **5**. Recrystallization from MeOH gave a sample which was identical with that isolated from catalytic reaction (*vide supra*).

Acknowledgment. One of us (R. Z.) wishes to thank the West German government for the award of a NATO Postdoctoral Fellowship, which made this study possible.

Registry No.—**1**, 1470-94-6; **2**, 5111-69-3; **3**, 707-95-9; **4**, 707-96-0; **5**, 50415-46-8; **5** picrate, 50415-47-9; **11**, 50415-48-0; **12**, 50415-49-1; methanol, 67-56-1; 1,2,3,4-tetramethylbenzene, 488-23-3; methyl 3-bromoisobutyrate, 20609-71-6.

References and Notes

(1) (a) This investigation was supported by Research Grant No. CA-5969 from the National Cancer Institute, U. S. Public Health Service. (b) NATO Postdoctoral Fellow, 1966-1967. (c) On leave from the Department of Chemistry, Weizmann Institute of Science, Rehovoth, Israel, 1964-1969.

(2) (a) L. H. Klemm, J. Shabtai, and D. R. Taylor, *J. Org. Chem.*, **33**, 1480 (1968); (b) *ibid.*, **33**, 1489 (1968); (c) *ibid.*, **33**, 1494 (1968); (d) *ibid.*, **35**, 1075 (1970).

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(5) For simplicity, catalysts are designated by the same capital letters, respectively, as used in earlier papers.[2,3] For determination of acidities of these catalysts see ref 2a and papers cited therein.

(6) Elemental analyses were performed by Micro-Tech Laboratories, Skokie, Ill. Infrared spectra were obtained by means of a Beckman IR-7 spectrometer; pmr spectra by means of a Varian Associates A-60 instrument, with tetramethylsilane as internal reference; and ultraviolet spectra by means of a Cary 15 spectrophotometer.

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(12) The methyl signals occur as overlapping singlets in the region δ 2.2-2.3.

(13) *Cf.* values of 1705-1710 cm^{-1} for indanone and methyl-substituted indanones: "Sadtler Standard Infrared Spectra Catalog," Spectra No. 3426, 4890, 14324.

(14) The methyl signals occur as overlapping singlets in the region δ 2.1-2.3.

Noble Metal Catalysis. III. Preparation of Dialkyl Oxalates by Oxidative Carbonylation

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Dialkyl oxalates can be prepared in good yields by oxidative carbonylation in the presence of alcohols and dehydrating agents using a palladium redox system and oxygen. The other product, water, is removed by the dehydrating agent. If the dehydrating agent is not effective, then large amounts of carbon dioxide are made and no oxalates are found. At low carbon monoxide pressure increased amounts of dialkyl carbonate are also found. Of the various cocatalysts tried, a cupric chloride-cuprous chloride system was found to be the most selective.

Dialkyl oxalates can be prepared in good yields by oxidative carbonylation[1] in the presence of alcohol and dehydrating agents using a palladium redox system according to eq 1 and 2.

$$2CO + 2ROH + \tfrac{1}{2}O_2 \longrightarrow RO_2CCO_2R + H_2O \qquad (1)$$

$$H_2O + (RO)_3CH \longrightarrow 2ROH + HCO_2R \qquad (2)$$

The dehydrating agent is necessary; otherwise large amounts of carbon dioxide are produced and no oxalates are found. The palladium redox system is somewhat similar to the one used in acetaldehyde synthesis,[2] but optimum results are achieved by restricting the amounts of chloride ion. In addition, carbonates are produced by much the same chemistry.

Results

The major products of the reaction are oxalates and carbonates, but, in addition, there are also produced under some conditions significant amounts of carbon dioxide and esters arising from solvent attack. Under acidic conditions some alkyl halides and ethers are also produced. Table I shows some of the results concerning the synthesis of diethyl oxalate using two of the three useful cocatalysts, iron and copper halides. An example of the third cocatalyst type, the quinones, is shown in the Experimental Section.

A comparison of runs 1 and 3 shows that although ferric chloride gives much the better ratio of oxalate to carbonate than does cupric chloride, ferric chloride causes the

Table I
Synthesis of Diethyl Oxalate

Run	Cocatalyst[a]	Millimoles of cocatalyst	Initial pressure of carbon monoxide, psig	Mol % yield, carbonate plus oxalate to total yield	Mole ratio		
					Oxalate to carbonate	Oxalate plus carbonate to CO_2	Oxalate plus carbonate to acetate
1	$FeCl_3$	62	1000	31	2.5	5.7	0.49
2	$FeCl_3$ LiCl	62 71	1000	23	0.27	0.40	1.1
3	$CuCl_2$	37	1000	81	1.4	5.6	18
4	$CuCl_2$ LiCl	37 118	1000	31	0.44	2.3	0.57
5	$CuCl_2$ LiCl	36 118	500	72	0.14	5.0	5.3
6	$FeCl_2$ HCl	47 28	1000	35[c]	2.6		0.55
7	$FeCl_2$ LiCl	62 62	1000	37	0.41	4.5	0.66
8	$FeCl_3$ NaOAc	62 74	1000	30	1.4	1.2	0.64
9	$CuCl_2$ $Cu(OAc)_2$	35 30	1000	92[c]	1.4		12
10	$CuCl_2$ Cu_2Cl_2	35 50	1000	93[c]	2.4		>40
11	$FeCl_3$ $PdCl_2$	22 17	1000	35[c]	0.53		0.54
12[b]	$CuCl_2$ Cu_2Cl_2	35 30	500		0.52		
13[b]	$CuCl_2$ Cu_2Cl_2	35 30	1000		1.3		

[a] With 6 mmol of $PdCl_2$ (except where noted), 200 ml of absolute ethanol, and 200 ml of triethyl orthoformate in a stirred 0.5-gal autoclave and oxygen addition in 10–20-psig increments until a total of 150–500 psig had been added, temperature 125°. [b] Using methanol and trimethyl orthoformate instead of ethanol and triethyl orthoformate. [c] Carbon dioxide yield not included.

production of large amounts of ethyl acetate. The production of ethyl acetate is quite severe for all of the iron runs and is consistent with the fact that the iron halides, independent of palladium, are known to oxidize ethanol to acetaldehyde and finally to ethyl acetate.[3] The effect of additional chloride can be seen in runs 2 and 4. The addition of chloride decreases the ratio of oxalate to carbonate for both iron and copper and decreases the ratio of oxalate plus carbonate to carbon dioxide. Also the attack on solvent in run 4 is severe. The effect of acids and bases can be seen in runs 6–9. Run 6 might be expected to give similar results to run 1 as long as the oxidation of $FeCl_2$ is reasonably complete, according to eq 3, and such was found

$$2FeCl_2 + 2HCl + \tfrac{1}{2}O_2 \longrightarrow 2FeCl_3 + H_2O \qquad (3)$$

to be the case. In run 7 the effect of base is seen. To the extent that eq 3 proceeds to the right then in this case an equivalent of base is produced. Since the results of this experiment are not as satisfactory as compared to run 1, then the presence of base must be deleterious. This is further seen in run 8, where NaOAc (which is not as strong a base as lithium ethoxide) also brings the oxalate to carbonate ratio down. The presence of copper acetate in run 9 creates two effects. It removes excess chloride, which is indicated in run 10 to be highly beneficial, but it also increases the amount of base which is detrimental. Run 10 shows that the addition of cuprous chloride is highly beneficial. No attack on solvent was discernible. The actual concentration of cuprous chloride is unknown, since cuprous chloride is somewhat insoluble. Run 11 shows that most of the palladium is not in the oxidized form because the liberated chloride makes run 11 more like run 2 rather than like run 1.

Table I shows the effects of increasing the carbon monoxide pressure from 500 to 1000 psig (runs 4, 5, 12, 13). In both sets there is a significant increase in the oxalate–carbonate ratio. On the other hand, an increase in the pressure of carbon monoxide leads to higher rates of production of carbon dioxide and ethyl acetate.

If oxygen is not used then water is not formed and it is not necessary to use dehydrating agents. Such is the case where benzoquinone alone is used as the oxidant, as shown in the Experimental Section, although orthoformates are beneficial.

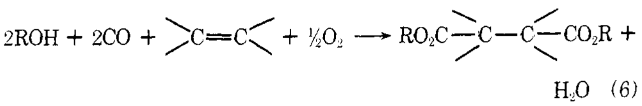
Discussion

Although the equations for the regeneration reactions for the catalyst system[4] are frequently described (for copper) as in eq 4 and 5, it may be that these reactions do

$$Pd^0 + 2CuCl_2 \longrightarrow Cu_2Cl_2 + PdCl_2 \qquad (4)$$

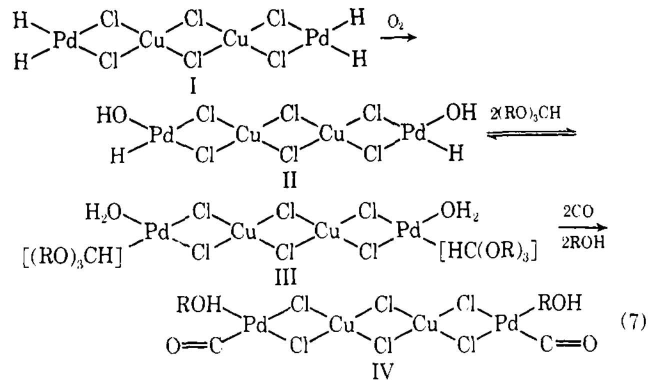
$$Cu_2Cl_2 + 2HCl + \tfrac{1}{2}O_2 \longrightarrow 2CuCl_2 + H_2O \qquad (5)$$

not occur in discrete steps. If the reactions were discrete steps, then the liberation of water according to eq 5 would occur independently of palladium so that at least some of the time palladium(II) might be expected to react as if no water was present. However, it was already seen that orthoformates are necessary for oxalate production, though even in the presence of orthoformates some carbon dioxide is obtained. It was therefore concluded that the water molecule is an important ligand coordinated to palladium. This conclusion is consistent with the fact that water was shown to have a pronounced influence in the oxidation of olefins to succinates[5] as illustrated in eq 6.



$$2ROH + 2CO + {>}C{=}C{<} + \tfrac{1}{2}O_2 \longrightarrow RO_2C{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}CO_2R + H_2O \qquad (6)$$

Since either iron or copper halides or quinones are necessary for sustained reaction, it is concluded that these materials complex to palladium. Therefore the following complex, I, is postulated as the reduced species (for copper) and the following reactions illustrate its oxidation.



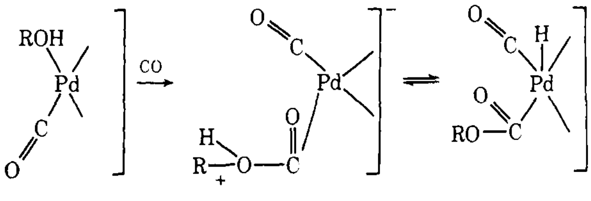
(7)

The oxygen atoms can be transferred by epoxide-type bridges between metal atoms or possibly by hypohalite exchanges, although hypohalite-type oxidation products are found only when quite high concentrations of copper are used.[6] The need for two palladium atoms in complex I is deduced from the fact that if only one was present, then two molecules of water (from O_2) would eventually come from a single palladium, which demands that the second palladium would not have an initial water ligand, so that some oxalate and carbonate should be formed in the absence of dehydrating agent. Two cuprous chlorides are used because in that way the addition or subtraction of halide ion as the complexes are oxidized and reduced is not necessary. It is postulated that there is an equilibrium between complexes having water in its dissociated form, II, and water in its undissociated form, III. It is proposed that the next advantageous step is the removal of the water ligand from the palladium. If this water is not removed then carbon dioxide is a likely product. Since the trialkyl orthoformate, under the conditions listed in Table I, is the only agent capable of water removal, then other ligands which compete favorably with the orthoformate should be kept to minimums. From Table I, it is seen that excess chloride ion increases the fraction of carbon dioxide synthesis. Also, from Table I, it can be seen that while increasing the carbon monoxide pressure from 500 to 1000 psig increased the oxalate to carbonate ratio it also increases the fraction of carbon dioxide made. Therefore carbon monoxide also impedes the formation of palladium-orthoformate bonds.

The orthoformate ligand can then react with the water ligand to give alcohol and alkyl formate. The question then arises as to whether it is the oxidation of two alkyl formates to dialkyl oxalates that is occurring instead of, or in addition to, the oxidation of carbon monoxide to oxalates. To answer this question methyl formate with trimethyl orthoformate was heated with palladium chloride using benzoquinone as a cooxidant in a closed system. Neither carbonate nor oxalate was found. In addition benzyl formate under oxidizing conditions in an open system was not consumed and benzoquinone was recovered unreacted. Also neither tributyl orthoformate nor trimethyl orthoformate gave carbonates or oxalates under oxidizing conditions.

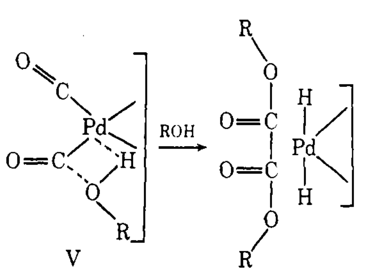
It is seen from Table I that cuprous chloride is highly beneficial and that most of the palladium is not in the Pd(II) oxidation state. All of these facts are consistent with the proposal that I is the main form of the redox system during oxalate synthesis. The same type of a complex can be written for ferrous chloride in place of cuprous if the additional two chlorides are both placed on the same side of the otherwise planar ring systems. The oxygen can then migrate on the opposite side.

Proposed Mechanism of Oxalate Formation. Several palladium carbonyl complexes are known, including one containing two coordinated carbonyl ligands. Also palladium carboalkoxyl complexes are known.[7] Starting with complex IV it is envisioned that a carboalkoxyl ligand is formed, according to eq 8.



(8)

Any negative charge generated on palladium can also be expected to be stabilized by the attached copper ligands through the chloride bridges to the copper atoms. It is also possible that the hydrogen may occupy an intermediate site, *e.g.*, V. The attack of another alcohol molecule then triggers the production of oxalates.



(9)

Experimental Section

The reactions were carried out in either stainless steel or titanium autoclaves. The steel autoclaves sometimes exhibited excessive corrosion, particularly when excess halide ion was used. However, corrosion was much reduced when halide acceptors were used, such as cuprous chloride. Titanium parts are not advised since under anhydrous conditions with oxygen, titanium was shown to react, sometimes explosively, particularly in the oxygen inlet line, to give, at least in some cases, titanium tetraalkoxides. Teflon parts were found to be highly advantageous. The catalyst system and liquids were charged to the autoclave and carbon monoxide was added to the desired pressure. Stirring was commenced and the autoclave was heated to the desired temperature. Oxygen was then added (controlled from behind a suitable barricade) in 10-20-psig increments. In almost all cases an immediate exotherm was noted and cooling water was circulated to bring the temperature under control. Pressure drops were noted. Oxygen was added until 150-500 psig had been added or until the reaction slowed down. In those cases where no noticeable reaction occurred, no more than 40 psig oxygen was added. After oxygen addition the autoclave was cooled to room temperature and the gases were collected and analyzed by gas chromatography. The liquid was weighed and analyzed by gas chromatography and occasionally by distillation.

Oxalate Synthesis Using Benzoquinone as Sole Oxidant. A. With Triethyl Orthoformate. To 30 g of benzoquinone, 0.5 g of palladium chloride, 100 ml of ethanol, and 20 ml of triethyl orthoformate in a 300-ml capacity titanium bomb was added carbon monoxide to 1000 psig. The mixture was rocked and heated to 125° for 4 hr. The final pressure was 500 psig. The liquid product (94 g) contained 8.4 wt % ethyl carbonate and 1.49 wt % ethyl oxalate, or a mole ratio of oxalate to carbonate of 1.4.

B. With Triethyl Orthoacetate. To 20 g of benzoquinone, 0.5 g of palladium chloride, 70 ml of anhydrous ethanol, and 30 ml of triethyl orthoacetate in a 300-ml capacity stainless steel bomb was added carbon monoxide to 800 psig. The mixture was rocked and heated to 125° for 4 hr. The liquid product (75 g) contained 0.5 wt % diethyl carbonate and 1.9 wt % diethyl oxalate. No ethyl formate was noted.

C. No Drying Agent. To 20 g of benzoquinone, 70 ml of anhydrous ethanol, and 0.5 g of palladium chloride in a 300-ml capacity stainless steel bomb was added carbon monoxide to 800 psig. The mixture was rocked and heated to 125° for 4 hr. The liquid product (55 g) contained 1.1 wt % diethyl carbonate and 1.2 wt % diethyl oxalate. No ethyl formate was noted.

Registry No.—Diethyl oxalate, 95-92-1; $FeCl_3$, 7705-08-0; LiCl, 7447-41-8; $CuCl_2$, 7447-39-4; $FeCl_2$, 7758-94-3; HCl, 7647-01-0;

NaOAc, 127-09-3; Cu(OAc)$_2$, 142-71-2; Cu$_2$Cl$_2$, 12258-96-7; PdCl$_2$, 7647-10-1.

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Conformational Analysis. XCIX. The 1-Decalone Ring System[1,2]

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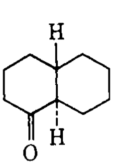
The equilibrium point for the isomerization of the 5α- and 5β-cholestan-4-ones has been redetermined to be 87 ± 1% 5α in ethanol at 25°, and earlier conflicting reports have been resolved. For the model 10-methyl-1-decalone system, the trans isomer is reported to be slightly favored at equilibrium, while, for the 9-methyl-1-decalone system, the cis isomer is favored. All of these results are well reproduced by a molecular mechanics calculation, and are discussed.

Twenty years ago Turner[3] was able to account quite well for the observed energy difference between *cis*- and *trans*-decalin, and to predict an energy difference between *cis*- and *trans*-9-methyldecalin (later verified experimentally[4,5]) in terms of the number of "gauche-butane"-like interactions in each isomer. The conformational analysis of decalone systems has presented a greater challenge, as numerous interactions between the carbonyl moiety and the rest of molecule have to be allowed for, including changes in the ring geometry due to the introduction of a carbonyl group. Early vector analysis calculations by Corey and Sneen[6] showed that these changes were likely to be important.

Klyne[7] sought to provide a systematic analysis of the interactions involved in decalone systems in terms of "alkyl ketone effects." His predictions concerning the conformational energies of 2-decalone systems have been borne out by experiments and recent force-field calculations.[8] In 1-decalone systems (**1**-**9**) he was able to account for the observed[9] stability of *trans*-1-decalone (**1**) as compared to *cis*-1-decalone (**2**, **3**), and for the excess[10] of *cis*- (**5**, **6**) over *trans*-9-methyl-1-decalone (**4**) at equilibrium. However, he calculated the *cis*-(a)-10-methyl-1-decalone conformer (**9**) to be of lower energy than *trans*-10-methyl-1-decalone (**7**), while the trans isomer is found experimentally to be the more stable. Since that time several equilibration studies have been carried out on 1-decalone systems[11-16] and steroidal analogs.[17-26] Conformational preferences have been deduced from ORD[27] and nmr[28] data, and these results have been discussed in terms of alkyl ketone effects.[29] Difficulties have persisted, particularly in reconciling the results reported for 1-decalone with those for steroidal analogs.



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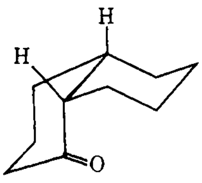

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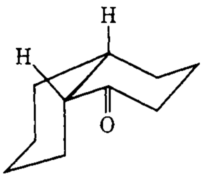

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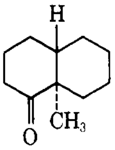
The advent of high-speed computers has permitted the application of molecular mechanics (or force-field) calculation methods to conformational problems. This approach explicitly allows for the relief of steric strain by



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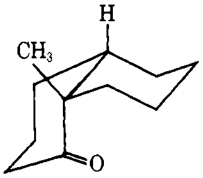

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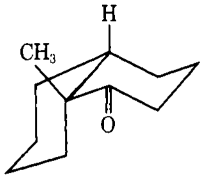

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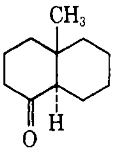

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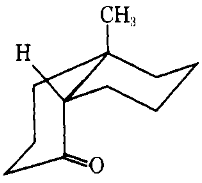

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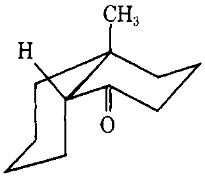

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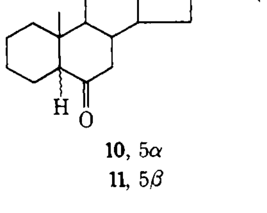
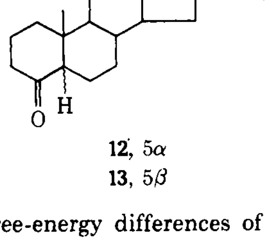
distortion, and permits quantitative analysis of complex systems. In earlier papers in this series the method has been developed and applied to hydrocarbons,[30] ketones,[31,32] and other types of structures. The force field used for the present work differs only trivially from that described earlier.[32] An initial study of the 10-methyl-1-decalone system (**7**, **8**, **9**) by this method[31] showed that the observed $\Delta G°$ trans $\rightleftharpoons$ cis of ~0.2 kcal[14-16] could be accounted for.

In an earlier paper in this series[17] on the cis $\rightleftharpoons$ trans equilibria of cholestan-6-ones (**10**, **11**) and cholestan-4-ones (**12**, **13**), experimental free-energy differences of 1.2 and 2.1 kcal, respectively, were reported. These values stand in marked contrast to the small $\Delta G°$ found in the 10-methyl-1-decalone system (above), and the reported preponderance of the cis epimer of 9-methyl-1-decalone at equilibrium.[10] The cholestan-4-one equilibrium (**12**, **13**) can be considered to provide an experimental definition of



10, 5α
11, 5β



12, 5α
13, 5β