chloroform showed a broadened singlet at 9.50 ppm for the aldehyde proton. When this reaction was carried out under identical conditions using water in place of deuterium oxide, the crude reaction mixture showed a doublet for the aldehyde proton with J = 1.5 Hz. Under these conditions the starting aldehyde was recovered after column chromatography in 65% yield.

Registry No.—**1a,** 19916-80-4; **1a** (*p*-toluenesulfonate), 19955-02-3; **1b,** 19916-81-5; **1b** (*p*-toluenesulfonate), 19916-82-6; **3,** 19916-83-7; **5b** (acetate), 19933-74-5; 17-methylene-4,5-tetramethylene[2.2]paracyclophane, 19933-75-6; δ-[2.2]paracyclophanylbutyric acid methyl ester, 19933-76-7.

Acknowledgment.—The authors are indebted to Mr. Paul Kronlage who helped to prepare some of the starting materials. This research was supported by a National Science Foundation Grant to Tulane University. The Varian A-60 instrument used in this work was purchased with National Science Foundation funds. [2.2]Paracyclophane was generously supplied by Union Carbide Corp.

Selective Reductions. XIII. The Reaction of Δ^2-Cyclopentenones with Representative Complex Hydrides. Aluminum Hydride as a Selective Reagent for the Reduction of the Carbonyl Group in Δ^2-Cyclopentenones

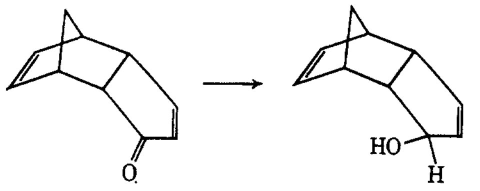
HERBERT C. BROWN AND HENRY M. HESS[1]

Richard B. Wetherill Laboratory of Purdue University, Lafayette, Indiana 47907

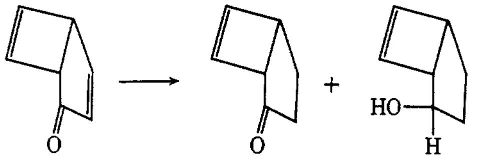
Received December 17, 1968

The reduction of 2-cyclopenten-1-one and 5,6-dihydro-*endo*-dicyclopentadien-1-one with metal hydrides takes place with considerable concomitant saturation of the double bond. However, the inverse addition of 0.667 mole equiv of aluminum hydride to 2-cyclopenten-1-one, 3-substituted 2-cyclopenten-1-ones, 5,6-dihydro-*endo*-dicyclopentadien-1-one, and 3-substituted 5,6-dihydro-*endo*-dicyclopentadien-1-ones, produces the unsaturated carbinols in satisfactory purity and yield and thus provides an effective route for the selective reduction of the carbonyl group in Δ^2-cyclopentenones.

The reduction of α,β-unsaturated ketones to the corresponding unsaturated carbinols with metal hydrides has often been reported to occur with varying amounts of concomitant saturation of the double bond, thereby affording saturated ketone and alcohol.[2,3] This mode of behavior is especially enhanced in Δ^2-cyclopentenones. Thus, while Woodward and Katz[4] reported that the reduction of *endo*-dicyclopentadien-1-one (I) with lithium aluminum hydride afforded the unsaturated alcohol II, Allara[5] and Dilling[6] have been unable to reproduce these results, obtaining substantial amounts of saturated products even at considerably reduced temperatures. Allara[5] has also reported that the reduction of 5,6-dihydro-*endo*-dicyclopentadien-1-one (VII) with lithium aluminum hydride and sodium borohydride produced substantial reduction of the double bond. Cookson[7] has reported that the reduction of *exo*-dicyclopentadien-1-one with lithium aluminum hydride yielded only the saturated alcohol. Story and Fahrenholtz[8] have demonstrated that *cis*-bicyclo[3.2.0]hepta-3,6-dien-2-one (III), when reduced with lithium tri-*t*-butoxyaluminohydride, gave, as the major product, *cis*-bicyclo[3.2.0]-6-hepten-2-one (IV) along with a small amount of the saturated alcohol V.[9-12] Paquette[13] has reported that the reduction of *cis*-bicyclo[3.2.0]hept-3-en-2-one with lithium aluminum hydride, even at −78°, afforded a complex mixture of products accompanying the desired unsaturated alcohol.



I II



III IV V

In view of these difficulties, and because a number of Δ^2-cyclopentenols were required for other work, a systematic study of the effect of metal hydrides on 2-cyclopenten-1-one (VI) and 5,6-dihydro-*endo*-dicyclopentadien-1-one (VII) was undertaken.

---

(1) Research assistant on grants (G 19878 and GP 6492 X) provided by the National Science Foundation.

(2) (a) N. Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publishers, Inc., New York, N. Y., 1956, pp 180–183; (b) V. M. Micovic and M. L. Mihailovic, "Lithium Aluminum Hydride in Organic Chemistry," Naukna Knjiga, Belgrade, Yugoslavia, 1955.

(3) P. L. Southwick, N. Latif, B. M. Fitzgerald, and N. M. Zaczek, *J. Org. Chem.*, **31**, 1 (1966), and references cited therein.

(4) R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

(5) D. L. Allara, Ph.D. Thesis, University of California, Los Angeles, 1964.

(6) W. L. Dilling, Britton Laboratory, Dow Chemical Co., private communication.

(7) R. S. Cookson, N. S. Isaacs, and M. Szelke, *Tetrahedron*, **20**, 717 (1964).

(8) P. R. Story and S. R. Fahrenholtz, *J. Amer. Chem. Soc.*, **87**, 1623 (1965).

(9) Lithium tri-*t*-butoxyaluminohydride, in contrast to lithium aluminum hydride and lithium trimethoxyaluminohydride, has previously been reported[10-12] to reduce cinnamaldehyde without attacking the double bond.

(10) F. A. Hochstein and W. G. Brown, *J. Amer. Chem. Soc.*, **70**, 3483 (1948).

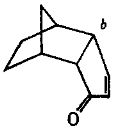
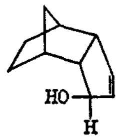
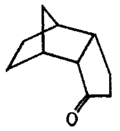
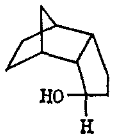
(11) H. C. Brown and P. M. Weissman, *ibid.*, **87**, 5614 (1965).

(12) H. C. Brown and P. M. Weissman, *Israel J. Chem.*, **1**, 430 (1963).

(13) L. A. Paquette and O. Cox, *J. Amer. Chem. Soc.*, **89**, 5633 (1967).

TABLE I

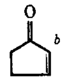
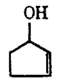
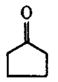
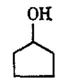
METAL HYDRIDE REDUCTIONS OF 5,6-DIHYDRO-*endo*-DICYCLOPENTADIEN-1-ONE[a]

Reagent	Solvent	Products, %			
		 [b]			
$LiAlH_4$	Et_2O[c]	31.3	13.8	28.3	26.6
$LiAlH_4$	Et_2O[c,d]	0	67	12.0	21.0
$LiAlH_4$	THF[e]	0	0	100	0
$LiAlH_4$	THF[e,f,m]	0	0	100	0
$LiAlH_4$	THF[g]	0	0	67.2	32.8
$LiAlH(OCH_3)_3$	THF[g]	45.0	42.0	9.6	3.4
$LiAlH(OCH_3)_3$	THF[h]	0	45.0	41.0	14.0
$LiAlH[OC(CH_3)_3]_3$	THF[g]	0	0	84.5	15.5
$NaBH_4$	EtOH[h]	0	0	0	100
AlH_3	THF[g]	0	66.6	14.2	19.2
AlH_3	THF[i]	0	65.8	32.7	1.5
AlH_3	THF[f,j]	0	84.6	7.1	8.3
AlH_3	THF[f,j,k]	0	86.0	10.0	4.0
AlH_3	THF[f,j,l]	27.3	64.3	5.9	2.5

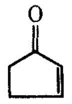
[a] Product analysis by glpc. Unless otherwise specified, the reaction consists of the normal addition of 1 mole of ketone to 1 mole of metal hydride. [b] Starting material. [c] 0.25 hr at 25°. [d] Reference 5. These results could not be reproduced. [e] 0.25 hr, 0°. [f] Inverse addition. [g] 17 hr at 0°. [h] 0.5 hr at 78°. [i] 1 hr at 0°. [j] 0.5 hr at 0°. [k] 0.667 mole equiv of reagent. [l] 0.33 mole equiv of reagent. [m] 0.25 mole equiv of reagent.

TABLE II

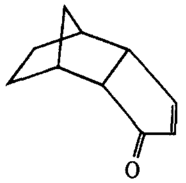
METAL HYDRIDE REDUCTIONS OF 2-CYCLOPENTEN-1-ONE[a]

Reagent	Solvent	Products, %			
		 [b]			
$LiAlH_4$	Et_2O[c]	[0	85	15	0
$LiAlH_4$	THF[d]	0	14.0	2.5	83.5
$LiAlH(OCH_3)_3$	THF[d]	0	90.5	0	9.5
$LiAlH[OC(CH_3)_3]_3$	THF[d]	0	0	11.2	88.8
$NaBH_4$	EtOH[e]	0	0	0	100
AlH_3	THF[f]	0	83.8	8.7	7.5
AlH_3	THF[f-h]	0	90.0	6.1	3.9

[a] Product analysis by glpc. Unless otherwise specified, the reaction consists of the normal addition of 1 mole of ketone to 1 mole of metal hydride. [b] Starting material. [c] At −10°, ref 5. [d] 17 hr at 0°. [e] 0.5 hr at 78°. [f] 0.5 hr at 0°. [g] Inverse addition. [h] 0.667 mole equiv of reagent.



VI



VII

Results and Discussion

2-Cyclopenten-1-one and 5,6-dihydro-*endo*-dicyclopentadien-1-one were reduced with lithium aluminum hydride, lithium trimethoxyaluminohydride, lithium tri-*t*-butoxyaluminohydride, sodium borohydride, and aluminum hydride. Tables I and II show that, with the exception of lithium trimethoxyaluminohydride and aluminum hydride, nearly exclusive saturation of the double bond resulted from the reaction of metal hydrides with these Δ^2-cyclopentanones under a variety of conditions.[14] The reduction of 3-methyl-2-cyclopenten-1-one with lithium aluminum hydride (inverse addition in THF, 0.5 hr at 0°) afforded 70% of the unsaturated carbinol and 30% of 3-methylcyclopentanol, demonstrating that while the presence of a 3 substituent decreases double bond saturation, such saturation still occurs.

The mechanism of double bond saturation is still uncertain,[2,3,5,8,10,15] but from the results in Table I, it is apparent that the unsaturated alcohol, once formed, is stable to the reaction conditions. Saturated alcohol, however, increases with time, indicating that, depending on the reagent, a metal hydride can add either 1,2 or 1,4 to the unsaturated ketone, the 1,4 attack then being followed by a slower reduction of the initially formed enolate. That similar results for these reductions were obtained with both 2-cyclopenten-1-one and 5,6-dihydro-*endo*-dicyclopentadien-1-one makes questionable the proposal by Story[8] that attack of hydride on the double bond is preferred in hindered cyclopentenones because the salt resulting from 1,2 *exo* attack of the reagent cannot be accommodated in the *endo* position.

---

[14] It should be noted that the effect of lithium tri-*t*-butoxyaluminohydride and lithium trimethoxyaluminohydride on the double bond of Δ^2-cyclopentenones differs from the effect reported[11,12] for cinnamaldehyde, indicating that the results with cinnamaldehyde, generally regarded as a model for reductions of α,β-unsaturated carbonyls, may not be general.

[15] M. E. Cain, *J. Chem. Soc.*, 3532 (1964).

Aluminum hydride[16,17] was found to be the most generally selective reagent for the selective reduction of the carbonyl group in Δ^2-cyclopentenones. The inverse addition of 0.667 mole equiv of aluminum hydride, prepared by the method previously described,[17] to 2-cyclopenten-1-one, 3-substituted 2-cyclopenten-1-ones, 5,6-dihydro-*endo*-dicyclopentadien-1-one, and 3-substituted 5,6-dihydro-*endo*-dicyclopentadien-1-ones has produced good yields of the corresponding unsaturated carbinols in excellent purity (see Table III). Consequently, this method provides an effective route for the selective 1,2 reduction of Δ^2-cyclopentenones, an important component of many polycyclic molecules.

Table III

Reduction of Δ^2-Cyclopentenones with Aluminum Hydride

Δ^2-Cyclopentenone	Carbinol, % purity	Carbinol, % yield
2-Cyclopenten-1-one	90.0[a]	79.0[a]
3-Methyl-2-cyclopenten-1-one	100[b]	76.2[c]
3-Phenyl-2-cyclopenten-1-one	100[b]	73[c]
5,6-Dihydro-*endo*-dicyclopentadien-1-one	86.0[a]	64.9[a]
3-Methyl-5,6-dihydro-*endo*-dicyclopentadien-1-one	100[b]	89.0[c]
3-Phenyl-5,6-dihydro-*endo*-dicyclopentadien-1-one	100[b]	92.5[c]

[a] Analysis by glpc. [b] Analysis by nmr. [c] Isolated yield.

Experimental Section

Δ^2-Cyclopentenones.—2-Cyclopenten-1-one, bp 150–152°, n^{20}_{D} 1.4795 (lit.[18] bp 151–154°, n^{20}_{D} 1.4810), 3-methyl-2-cyclopenten-1-one, bp 78–82° (20 mm), n^{20}_{D} 1.4842 (lit.[19] bp 74–76° (16 mm), n^{20}_{D} 1.4818), 3-phenyl-2-cyclopenten-1-one, mp 81–82.5° (lit.[20] mp 81–83°), and 5,6-dihydro-*endo*-dicyclopentadien-1-one, mp 49° (lit.[21] mp 50–51°), were prepared by the reported procedures. 3-Methyl-5,6-dihydro-*endo*-dicyclopentadien-1-one, bp 110–112° (3 mm), n^{26}_{D} 1.5262, and 3-phenyl-5,6-dihydro-*endo*-dicyclopentadien-1-one, mp 127.8–128.4, were also prepared[22] and will be reported in a later paper.

Table IV

Physical Properties of the Δ^2-Cyclopentenols

Δ^2-Cyclopentenols (registry no.)	Mp, °C	Formula	Calcd, %			Found, %		
			C	H	N	C	H	N
3-Methyl-2-cyclopenten-1-ol	Liquid[a]							
(*p*-nitrobenzoate) (19926-45-5)	91.5–92.5[b]	$C_{13}H_{13}NO_4$	63.15	5.30	5.67	63.24	5.48	5.66
3-Phenyl-2-cyclopenten-1-ol (19926-46-6)	103.3–105.3[c]	$C_{11}H_{12}O$	82.46	7.55		82.28	7.53	
5,6-Dihydro-*endo*-dicyclopentadien-*endo*-1-ol (19926-79-5)	103–105[b,d]	$C_{10}H_{14}O$	79.95	9.39		79.51	9.52	
3-Methyl-5,6-dihydro-*endo*-dicyclopentadien-*endo*-1-ol (19926-80-8)	79.4–79.9[b]	$C_{11}H_{16}O$	80.44	9.83		80.54	10.04	
3-Phenyl-5,6-dihydro-*endo*-dicyclopentadien-*endo*-1-ol (19926-81-9)	96–97[b]	$C_{16}H_{18}O$	84.91	8.02		85.01	8.24	

[a] Bp 70–71° (12 mm), n^{20}_{D} 1.4706. [b] Recrystallized from hexane. [c] Recrystallized from chloroform–hexane. [d] Reduction of 5,6-dihydro-*endo*-dicyclopentadien-1-one with aluminum deuteride, prepared from lithium aluminum deuteride, also produced the corresponding unsaturated deuterated alcohol.

General Procedure for the Reductions with Lithium Aluminum Hydride in THF.—Into a dry 50-ml round-bottom flask fitted with a magnetic stirrer and an injection port with a rubber syringe cap, were placed, under nitrogen, 2.1 ml of a 1.27 *M* lithium aluminum hydride solution in tetrahydrofuran (3.5 mmoles of $LiAlH_4$) and 10 ml of dry tetrahydrofuran. To this stirred solution, maintained at 0° in an ice bath, there was slowly added 3.5 mmoles of ketone in 10 ml of dry tetrahydrofuran. The mixture was stirred for the appropriate time, and then a 1:1 aqueous tetrahydrofuran solution was added slowly until no more hydrogen was evolved. After the addition of a standard naphthalene solution (to serve as an internal glpc standard), the reaction mixture was washed in a separatory funnel with a saturated solution of sodium potassium tartrate, and the tetrahydrofuran layer was dried ($MgSO_4$). The solution was concentrated by rotary evaporation and the product was examined by glpc. (For the inverse addition experiment, the procedure was appropriately altered.) For the bicyclic ketone, all analyses were carried out on a Perkin-Elmer 226 temperature-programmed capillary instrument fitted with a 150 ft × 0.01 in. Carbowax 20 M column. The saturated products were identified by comparison of the retention times with authentic samples.[23] For the 2-cyclopenten-1-one reductions, all analyses were carried out on a Perkin-Elmer 154 gas chromatograph fitted with a 3-ft column of Carbowax 20 M on Chromosorb W, HMDS treated.

Reduction of 5,6-Dihydro-*endo*-dicyclopentadien-1-one with Lithium Aluminum Hydride in Ether.—The procedure reported by Allara[5] was used. Ketone, 1 g, in 10 ml of anhydrous diethyl ether was added slowly from a dropping funnel into a stirred solution of 0.12 g of lithium aluminum hydride in 45 ml of dry diethyl ether contained in a 100-ml round-bottom flask previously flushed with nitrogen. After the addition was complete, the reaction was stirred for 15 min more. The mixture was hydrolyzed by adding successively 1 ml of water, 1 ml of 15% sodium hydroxide, and 5 ml of water. After the addition of a standard naphthalene solution, the mixture was filtered, washed once with water, and dried (K_2CO_3). The solution was concentrated by rotary evaporation and the product was examined by glpc.

General Procedure for the Reductions with Lithium Trimethoxyaluminohydride and Lithium Tri-*t*-butoxyaluminohydride.—Into a dry 50-ml round-bottom flask fitted with a magnetic stirrer and an injection port with a rubber syringe cap were placed, under nitrogen, 6.05 ml of a 1.65 *M* lithium aluminum hydride solution in tetrahydrofuran (40 mmoles of hydride) and 10 ml of dry tetrahydrofuran. To this stirred solution, maintained at the appropriate temperature, there was slowly added 30 mmoles of dry methanol (*t*-butyl alcohol). After the solution had reached thermal equilibrium, 2.5 mmoles of ketone in 4 ml of dry tetrahydrofuran was slowly added. The reaction mixture was stirred for the appropriate time and then slowly hydrolyzed with a 1:1 aqueous tetrahydrofuran solution. After the addition of a standard naphthalene solution, the mixture was washed in a separatory funnel with a saturated solution of sodium potassium tartrate, and the tetrahydrofuran layer was dried ($MgSO_4$). The solution was analyzed as before.

---

(16) M. J. Jorgenson, *Tetrahedron Letters*, 559 (1962).

(17) H. C. Brown and N. M. Yoon, *J. Amer. Chem. Soc.*, **88**, 1464 (1966); N. M. Yoon and H. C. Brown, *ibid.*, **90**, 2927 (1968).

(18) K. Alder and F. H. Flock, *Ber.*, **89**, 1732 (1956).

(19) R. M. Acheson and R. Robinson, *J. Chem. Soc.*, 1127 (1952).

(20) R. Riemschneider and R. Nerin, *Monatsh.*, **91**, 829 (1960).

(21) K. Alder and G. Stein, *Ann.*, **504**, 205 (1935).

(22) H. M. Hess, Ph.D. Thesis, Purdue University, 1969.

(23) H. C. Brown and I. Rothberg, unpublished data.

General Procedure for the Reductions with Sodium Borohydride.—Ketone, 5.0 mmoles, in 10 ml of ethanol was treated at room temperature with 10 mmoles of sodium borohydride in 10 ml of ethanol. After the exothermic reaction had ended (about 20 min), the mixture was heated on a steam bath for 10 min more. The reaction mixture was hydrolyzed with 25 ml of a 3% sodium hydroxide solution. After the addition of a standard naphthalene solution, the solution was extracted several times with ether, and the ether layer was dried ($MgSO_4$). The solution was concentrated by rotary evaporation and analyzed as before.

General Procedure for the Reductions with Aluminum Hydride.—Into a 50-ml round-bottom flask fitted with a magnetic stirrer and an injection port with a rubber syringe cap, were placed, under nitrogen, 2 mmoles of ketone in enough dry tetrahydrofuran to bring the total volume of the final solution to 10 ml. The solution was brought to 0° by means of an ice bath, and the appropriate amount of a standard aluminum hydride solution in tetrahydrofuran, prepared by the method of Brown and Yoon,[17] was added dropwise (for the normal addition experiments, the ketone was added slowly to the aluminum hydride solution). The mixture was stirred for the appropriate time at 0°. The hydrolysis and analysis procedures were the same as for the lithium aluminum hydride experiments.

General Procedure for the Preparative-Scale Reduction of Δ^2-Cyclopentenones.—The reduction of 3-methyl-2-cyclopenten-1-one is typical of the procedure used. Into a 1-l. round-bottom flask fitted with a magnetic stirrer and an injection port with a rubber syringe cap, was placed, under nitrogen, 10 g (104 mmoles) of 3-methyl-2-cyclopenten-1-one in 400 ml of dry tetrahydrofuran. The solution was brought to 0° by means of an ice bath and 90 ml of a 0.77 *M* aluminum hydride solution in tetrahydrofuran (69.3 mmoles of AlH_3) was added dropwise over a 15-min period. After the addition was complete, the reaction mixture was stirred at 0° for 30 min more and then hydrolyzed by adding successively 2.1 ml of water, 2.1 ml of 15% sodium hydroxide, and 6.3 ml of water. The aqueous layer was salted out with sodium carbonate and the aqueous layer was extracted with ether. The combined organic layers were washed with a saturated sodium bicarbonate solution and dried (K_2CO_3). Removal of the solvent by rotary evaporation afforded 8.5 g of liquid. Distillation of the liquid (12 mm) produced 7.8 g (79.5 mmoles, 76.2% yield) of carbinol. The physical properties of 3-methyl-2-cyclopenten-1-ol and the other Δ^2-cyclopentenols prepared by this procedure are recorded in Table IV.

Registry No.—Aluminum hydride, 1302-30-3.

Perhydroindan Derivatives. XI.[1a] The 7-Methoxyhexahydrofluorene System

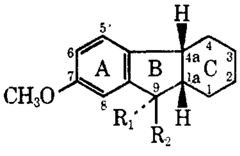
HERBERT O. HOUSE, THOMAS M. BARE,[1b] AND WILLIAM E. HANNERS

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

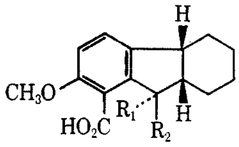
Received November 7, 1968

The known methoxyhexahydrofluorenone **6** has been converted into acids **1–4** desired as models for study of transformations in the aromatic ring. Of the various methods used to introduce the carboxyl functions, the selective lithium–hydrogen exchange and subsequent carbonation reactions applied to the olefins **10** and **35** and to alcohol **8** are worthy of special note.

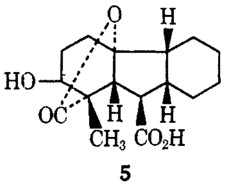
As part of our study of synthetic routes to the gibberellins,[2] we wished to study the acids **1–4** as model compounds for the transformation of the aromatic A ring into the nonaromatic system (*e.g.*, **5**) present in the gibberellins. This paper describes the preparation and interrelation of these model acids **1–4**.



1, $R_1 = CO_2H$; $R_2 = H$
2, $R_1 = H$; $R_2 = CO_2H$



3, $R_1 = CO_2H$; $R_2 = H$
4, $R_1 = H$; $R_2 = CO_2H$



5

The starting material for these acids was the known ketone **6** (Scheme I) prepared by acid-catalyzed cyclization[3] of the unsaturated ketone **7**. The formation of the ketone **6** under equilibrating conditions ensured the formation of the more stable diastereoisomer in which the B and C rings were *cis* fused.[3b] Reduction of the ketone **6** with $LiAlH_4$ yielded a single alcohol believed to have the stereochemistry indicated in structure **8** as a result of attack of the complex metal hydride anion from the less hindered side.[3c,4] Conversion of this alcohol **8** to the crude methanesulfonate ester followed by reaction with sodium cyanide yielded the olefin **9** rather than the desired nitrile. Olefin formation was more easily effected by brief acid-catalyzed dehydration to form the trisubstituted olefin **10** which was readily isomerized to the tetrasubstituted olefin **9**.

The acids **1** and **2** were most efficiently prepared by conversion of the olefin **10** (or mixtures of **9** and **10**) to the allylic lithium reagent which was carbonated to form the unsaturated acid **11** accompanied by small amounts of the isomeric acid **12**. Hydrogenation of the unsaturated acid **11** yielded the acid **1** as a result of the *cis* addition of hydrogen from the less hindered side of the olefin **11**. The methyl ester **13** of acid **1** could be epimerized and then hydrolyzed to yield the more stable C-9 epimer in which the carboxyl function is *trans* to the methylene groups of ring C.

An alternative route (Scheme II) to the acid **2**, although less efficient, provided evidence that the B–C ring fusion in acids **1** and **2** was *cis*. In this sequence the ketone was converted to olefins **15** and **16** by reaction with the appropriate Wittig reagents. Hydrolysis of the enol ether **15** (mixture of geometrical isomers) afforded the aldehyde **17** which was oxidized to the acid **2**. Hydroboration of the olefin **16** proceeded by attack from the less hindered side to yield, after oxidation, the

---

[1] (a) This research has been supported by Research Grant No. GP-5685 from the National Science Foundation and by Public Health Service Grant No. 1-R01-CA10933-01 from the National Cancer Institute. (b) National Institutes of Health Predoctoral Fellow, 1965–1968.

[2] For leading references, see (a) H. O. House, F. J. Sauter, W. G. Kenyon, and J. J. Riehl, *J. Org. Chem.*, **33**, 957 (1968); (b) H. O. House, J. K. Larson, and H. C. Müller, *ibid.*, **33**, 961 (1968).

[3] (a) W. G. Dauben and J. W. Collette, *J. Amer. Chem. Soc.*, **81**, 967 (1959); (b) H. O. House, V. Paragamian, R. S. Ro, and D. J. Wluka, *ibid.*, **82**, 1457 (1960); (c) H. O. House, V. Paragamian, and D. J. Wluka, *ibid.*, **82**, 2561 (1960).

[4] H. O. House, R. G. Carlson, H. Müller, A. W. Noltes, and C. D. Slater, *ibid.*, **84**, 2614 (1962).