was obtained in 71% yield after purification by sublimation, mp 120–123° (lit.[5] mp 121.5–124°). The nmr spectrum is in good agreement with that published.[5]

A *p*-nitrobenzoate was prepared according to the procedure given under *endo*-**2**, mp 101–103° (lit.[10] mp 106–107°).

3-Bicyclo[3.3.1]nonyl Acetates.—For the glpc analysis the *exo*- and *endo*-**3** mixtures were converted into the acetates. The alcohol mixture (*ca.* 100 mg) was mixed with 20 mg of anhydrous sodium acetate and 200 mg of acetic anhydride and the reaction mixture was heated for 2 hr at 100°. Ice (5 g) was added to the mixture and the product was taken up in pentane. The solution was dried ($MgSO_4$) and concentrated. Analysis was made *via* glpc as described below. Four independent runs on a sample containing 5.9% *endo*-**3** and 94.1% *exo*-**3** by weight gave 5.5 94.5, 5.6:94.4, 5.7:94.3, and 5.7:94.3%.

exo-**3-Bicyclo[3.3.1]nonyl Acetate.**—A sample of pure *exo*-**3** was acetylated as described above. The acetate was recovered by removal of the pentane: ir (neat) 1730, 1360, 1240, 1090 and 1030 cm^{-1}; nmr (CCl_4) δ 5.4 (m), 1.95 (s), and 0.8–2.4 (m).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 72.49; H, 9.95. Found: C, 72.70; H, 10.06.

endo-**3-Bicyclo[3.3.1]nonyl Acetate.**—A sample of the *endo* acetate prepared as above showed ir (neat) 1735, 1370, 1240, 1080, and 1010 cm^{-1}; nmr (CCl_4) δ 4.9 (m) and 0.7–2.5 (m).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 72.49; H, 9.95. Found: C, 72.57; H, 10.06.

Equilibration.—Those equilibrations using Raney nickel as a catalyst used solvents and catalyst prepared as described by Eliel and Schroeter.[8] A solution containing *ca.* 100 mg of the appropriate alcohol in 2–3 ml of solvent was mixed, with the catalyst (1–3 g) and sealed in a glass tube. The tube was suspended in a constant-temperature bath until equilibration (as determined from a series of check samples) was complete. The reaction was terminated by removal of the sample from the bath and after opening of the tube by removal of the catalyst by filtration. The catalyst was washed thoroughly and the solvent was removed by distillation. Analysis was made by glpc, and in most cases at least two runs were made from each side of the equilibrium. In the case of the 3-bicyclo[3.3.1]nonanols, the crude mixture was converted into the acetates prior to analysis as described above.

Reagents and solvents for equilibrations using aluminum isopropoxide were prepared as described by Eliel and Schroeter.[8] Equilibrations were carried out on 100 mg of the alcohol with 110 mg of aluminum isopropoxide in 1–2 ml of isopropyl alcohol containing 10–20 μl of acetone. A sealed-tube technique was used as described above. After equilibration had been completed, the contents of the reaction tube were poured into 5 ml of 0.7 *N* hydrochloric acid and the product was taken up in pentane. The pentane solution was dried (K_2CO_3) and used for analysis.

Analyses.—All analyses were carried out on an Aerograph 204B equipped with flame ionization detector and an L & N type W recorder with a Disc integrator. Mixtures of *exo*- and *endo*-**2** were analyzed directly using a 12 ft × 0.125 in. 5% FFAP on Chromosorb G column at 125°. The *exo*- and *endo*-**3** were converted into the acetates as described above and analyzed on a 100-ft capillary column with MBMA as a liquid phase at 125°. Peak areas indicated by the Disc integrator were checked by counting squares on the graph. All analyses were made in duplicate and the value reported is an average of the two (Table I).

TABLE I
RESULTS OF EQUILIBRATION STUDIES

Run	Reactant	Catalyst	Solvent	Time, days	Equilibrium mixture, *exo*/*endo*
1	*endo*-**3**	Al-*i*-PrO	*i*-PrOH	20	96.8:3.2
2	*endo*-**3**	Al-*i*-PrO	*i*-PrOH	20	96.9:3.1
3	*exo*-**3**	Al-*i*-PrO	*i*-PrOH	20	97.1:2.9
4	*exo*-**3**	Al-*i*-PrO	*i*-PrOH	23	96.7:3.4
5	*exo*-**2**	Al-*i*-PrO	*i*-PrOH	20	30.8:69.2
6	*endo*-**2**	Al-*i*-PrO	*i*-PrOH	20	31.3:68.7
7	*exo*-**2**	Raney Ni	*i*-PrOH	8	32.1:67.9
8	*endo*-**2**	Raney Ni	*i*-PrOH	8	31.2:68.8
9	*exo*-**2**	Raney Ni	C_6H_{12}[a]	10	41.0:59.0
10	*exo*-**2**	Raney Ni	C_6H_{12}	10	41.0:59.0
11	*exo*-**2**	Raney Ni	C_6H_{12}	10	39.6:60.4
12	*endo*-**2**	Raney Ni	C_6H_{12}	10	42.0:58.0
13	*endo*-**2**	Raney Ni	C_6H_{12}	10	39.8:60.2
14	*b*	Raney Ni	*i*-PrOH	2	30.6:69.4
15	*b*	Raney Ni	C_6H_{12}	3.5	32.0:68.0

[a] Cyclohexane. [b] 2-Bicyclo[3.3.1]nonanone.

Registry No.—*exo*-**2**, 22485-97-8; *endo*-**2**, 10036-25-6; *exo*-**3**, 10036-10-9; *endo*-**3**, 10036-08-5.

Synthesis of Bicyclo[3.3.1]nonanes. Products of the Friedel–Crafts Reaction of 3-(3-Cyclohexen-1-yl)propionyl Chloride[1]

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A series of bicyclo[3.3.1]nonane derivatives can be prepared by a Friedel–Crafts reaction of 3-(3-cyclohexen-1-yl)propionyl chloride (**2**) under various conditions. Stannic chloride in chloroform gives 7-bicyclo[3.3.1]nonen-2-one (**3**) and 8-chloro-2-bicyclo[3.3.1]nonanone (**4**). Aluminum chloride in 1,2-dichloroethane leads to 6-chloro-2-bicyclo [3.3.1]nonanone (**7**), which can be converted into 6-bicyclo[3.3.1]nonen-2-one (**8**). With aluminum chloride in boiling cyclohexane, **2** gives 2-bicyclo[3.3.1]nonanone (**6**). Finally, 3-(3-cyclohexen-1-yl)propionic acid (**1**) gives 2,3,4,5,6,7-hexahydro-1-indenone (**9**) when treated with polyphosphoric acid.

Interest in the bicyclo[3.3.1]nonane ring system has been revived recently, in part because it is of importance in the synthesis of some complex natural products,[4] and in part because it presents an interesting skeleton for mechanistic studies.[5] This interest has promoted development of some novel and useful syntheses of the ring system,[6] but most of these are best adapted to the preparation of molecules substituted in a single ring. The preparation of bicyclo[3.3.1]nonanes with

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(2) Petroleum Research Fund Fellow, 1966–1968.

(3) Petroleum Research Fund Fellow, 1963–1964.

(4) J. Martin, W. Parker, and R. A. Raphael, *Chem. Commun.*, 633 (1965); R. O. H. Murray, W. Parker, and R. A. Raphael, *Tetrahedron*, **16**, 74 (1961).

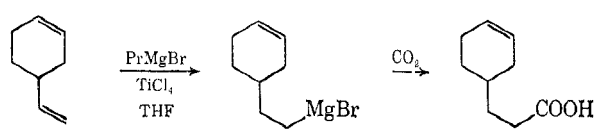
(5) See, for example, the following papers and preceding papers in each series: (a) J. M. Davies and S. H. Graham, *J. Chem. Soc.*, 2040 (1968); (b) M. A. Eakin, J. Martin, and W. Parker, *Chem. Commun.*, 298 (1968); (c) J. P. Schaefer and C. A. Flegal, *J. Amer. Chem. Soc.*, **89**, 5729 (1967); (d) E. N. Marvell, G. J. Gleicher, D. Sturmer, and K. Salisbury, *J. Org. Chem.*, **33**, 3393 (1968).

(6) G. Stork and H. K. Landesman, *J. Amer. Chem. Soc.*, **78**, 5129 (1956); S. Brewis and P. R. Hughes, *Chem. Commun.*, 6 (1966); E. F. Knights and H. C. Brown, *J. Amer. Chem. Soc.*, **90**, 5283 (1968).

substituents in both rings is still dominated[7] by the classic synthesis of Meerwein.[8] We have now developed an economical and versatile synthesis for bicyclo[3.3.1]nonanes bearing different functionality in each of the rings.

Earlier work[9] had shown that the "ene participation" route to bicyclo[3.3.1]nonanes is not synthetically useful. However, the great simplicity and potential versatility of the route prompted us to examine further variants which might prove effective. One reasonable possibility was internal acylation, a process used successfully for the formation of bicyclic ketones,[10] albeit normally for *ortho*-fused rings. After the present work had been completed, Erman and Kretschmer[11] showed that 4-cyclooctenecarbonyl chloride gives 2-chlorobicyclo[3.3.1]nonan-9-one.

The synthesis of 3-(3-cyclohexen-1-yl)propionic acid (**1**) was accomplished initially by conventional elaboration of the side chain in 3-cyclohexene-1-carboxaldehyde. However, the elegant procedure of Finkbeiner and Cooper[12] was modified to provide a single-step path to the desired acid in *ca.* 50% yield from 4-vinylcyclohexene.



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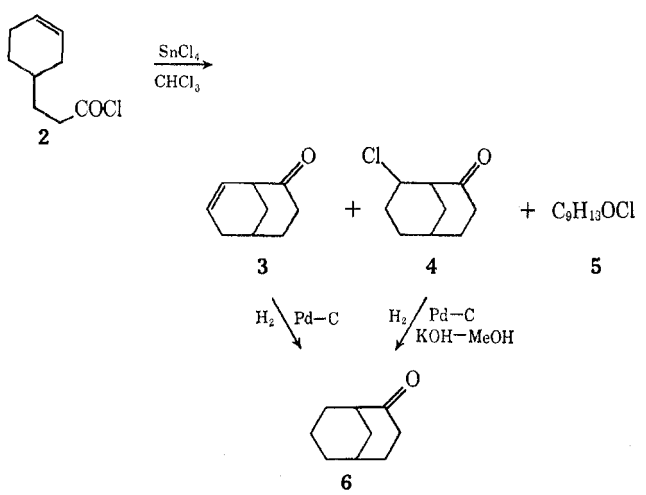
Acylation with Stannic Chloride.—The first attempts to induce 3-(3-cyclohexen-1-yl)propionyl chloride (**2**) to undergo an internal acylation were carried out with stannic chloride in chloroform. Three products were isolated from the reaction: an unsaturated ketone (**3**) and two monochloro ketones (**4** and **5**). Enone **3**, mp



2 3 4 5 6

66–68°, was characterized spectrally: uv, λ_{max} 298 nm (ϵ 180) and 202 (2100); ir, 1710 cm^{-1} (ketone); nmr, two olefinic protons at 5.5–6.2 ppm and particularly a single-proton resonance centered at 2.8 ppm.[5d] Cyclization would be expected to lead to 7-bicyclo[3.3.1]-nonen-2-one (**3**) or to 6-bicyclo[3.2.2]nonen-2-one, a known substance.[13] The latter was eliminated, since it has λ_{max} 288 and 214 nm and nmr and mass spectra clearly different from the product isolated in our reaction. The assignment of a bicyclo[3.3.1]nonane skeleton to our product was confirmed by reduction of **3** to the known ketone **6**.[14] However, the position of the double bond is not necessarily as shown despite the synthetic route, since Colvin and Parker[15] have shown that double bonds in the bicyclo[3.3.1]nonane system may migrate under acid conditions. The presence of a proton resonance at 2.8 ppm in the nmr spectrum of **3**, which can be assigned to the bridgehead proton at C_1, suggested that the 7 position was correct. This was confirmed by the synthesis of 6-bicyclo[3.3.1]-nonen-2-one (**8**) (see below), which has no bands in this region. Despite its apparent purity, **2** could contain small amounts of **8**, since we would probably be unable to detect 5–10% **8** in our sample.

Of the two monochloro ketones, one has been tentatively identified as 8-chlorobicyclo[3.3.1]nonan-2-one (**4**). Catalytic reduction of **4** under basic conditions gave **6** which delineates the carbon skeleton. The synthetic scheme suggests that the chlorine should be at C_8, but later results (see below) showed that chlorine migration occurs readily. Dehydrohalogenation should provide an unequivocal assignment, since an 8 Cl should give exclusively **3**, while a 7 Cl should give a mixture of **3** and **8**. Dehydrohalogenation proved difficult. Tertiary amines gave poor yields of complex mixtures, and silver ion led to a mixture of **3** and a second product having ν_{CO} at 1755 cm^{-1}. We have been unable to separate the mixture, but the presence of **3** can be confirmed spectrally. Furthermore, the CHCl resonance in the nmr spectrum of **4** is markedly different from those of a CHOH at C_3. Thus we consider that the chlorine is attached to C_8, but whether it is *exo* or *endo* is not yet established.

The third product (**5**) is characterized by a carbonyl band at 1710 cm^{-1} and a proton resonance at 4.4 ppm, suggesting the presence of a CHCl unit. The compound analyzes correctly for $C_9H_{13}OCl$ and is monomeric (mass spectrum). However, all attempts to remove the halogen reductively in order to determine the nature of the carbon skeleton have been unsuccessful. Thus no structural assignment can be made at present.

Influence of Conditions on Yields.—In order to improve the yield of **3**, a relatively comprehensive study of the influence of catalyst and solvent on the Friedel–Crafts reaction of **2** was made. The results of glpc analysis of the products obtained are shown in Table I. The data disclose a remarkable sensitivity of the nature of the product to both catalyst and solvent. Since the bicyclic products are generally difficult to isolate and purify, only those conditions which lead to relatively simple mixtures were selected for further study. Aside from the stannic chloride–chloroform

(7) J. P. Schaefer and L. M. Honig, *J. Org. Chem.* **33**, 2655 (1968).
(8) H. Meerwein, F. Kiel, G. Klosgen, and E. Schoh, *J. Prakt. Chem.*, [2] **104**, 161 (1922).
(9) E. N. Marvell, D. Sturmer, and R. S. Knutson *J. Org. Chem.*, **33**, 2991 (1968).
(10) J. W. Cook and C. A. Lawrence, *J. Chem. Soc.*, 1637 (1938); J. C. Bardhan and K. C. Bhattacharyya, *Chem. Ind.* (London), 800 (1953); D. W. Mathieson, *J. Chem. Soc.*, 3251 (1953); P. A. Plattner and G. Büchi, *Helv. Chim. Acta*, **29**, 1608 (1946).
(11) W. F. Erman and H. C. Kretschmer, *J. Org. Chem.*, **33**, 1545 (1968).
(12) H. L. Finkbeiner and G. D. Cooper, *ibid.*, **27**, 3395 (1962).
(13) J. A. Berson and M. Jones, Jr., *J. Amer. Chem. Soc.*, **86**, 5019 (1964). We are indebted to Professor Berson for a sample of this ketone.
(14) E. N. Marvell, D. Sturmer, and C. Rowell, *Tetrahedron*, **22**, 861 (1966), and references cited therein.
(15) E. W. Colvin and W. Parker, *J. Chem. Soc.*, 5764 (1965).

TABLE I

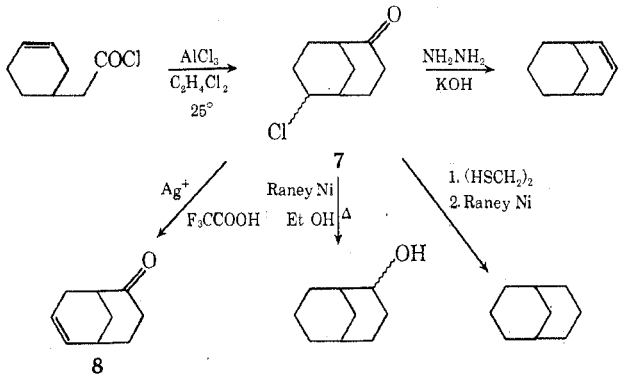
RESULTS OF THE ANALYSIS OF FRIEDEL–CRAFTS PRODUCTS FROM 2 UNDER VARIOUS CONDITIONS

Catalyst	Solvent	Per cent area under peak[a] A[b]	B[c]	C[b]	D[b]	E[b]	F[d]	G[b]	H[e]	I[b]
$SnCl_4$	$ClCH_2CH_2Cl$		40			5	29		13	14
	$CHCl_3$		48			5	17	4		26
	CH_2Cl_2		43			5	28		9	16
	CS_2		33			7	42		10	8
$AlCl_3$	$ClCH_2CH_2Cl$		3	2	2	6	21		63	4
	CCl_4		6	6	28	16	17		19	2
	$CHCl_3$		6		5	12	44		27	6
	CS_2		7	7	28	20	18		19	2
	C_6H_{12}	37	52[f]			2	4	2		4
$ZnCl_2$[g]	$CHCl_3$		50			11		30		7
	CH_2Cl_2		36					57		7
$FeCl_3$	$ClCH_2CH_2Cl$		29				14	20	42	6
	$CHCl_3$		17				56		17	10
	CS_2		5	3			22	22	44	4
$TiCl_4$	CCl_4		7	←	10	→	61		10	6
	CS_2		15	←	13	→	56		5	12

[a] The peaks are lettered in order of elution. [b] The substance responsible for this peak has not been identified. [c] This component is 7-bicyclo[3.3.1]nonen-2-one (**3**). [d] This component is 8-chlorobicyclo[3.3.1]nonan-2-one (**4**). [e] This component is 6-chlorobicyclo[3.3.1]-nonen-2-one (**7**). [f] This component is 2-bicyclo[3.3.1]nonanone (**6**). [g] Reactions with $ZnCl_2$ were slow and these results represent incomplete reaction.

system already considered for the preparation of **3**, the use of aluminum chloride–dichloroethane for the preparation of the compound responsible for peak H, of aluminum chloride–cyclohexane for the synthesis of **6**, and of titanium chloride–dichloroethane for formation of **4** were examined further.

Acylation with Aluminum Chloride–Dichloroethane.—As is indicated in Table I, the use of aluminum chloride in dichloroethane converts **2** mainly into one compound elected as peak H. This product is another monochloro ketone, $C_9H_{13}OCl$, which has been assigned the structure of 6-chloro-2-bicyclo[3.3.1]nonanone (**7**) on the basis of the data described below. It was



isolated routinely in yields of 40% on a preparative scale. Removal of the chlorine atom by reductive means proved difficult, but was ultimately accomplished in two ways. Wolff–Kishner reduction gave a crystalline hydrocarbon which proved identical with 2-bicyclo[3.3.1]nonene.[16] Raney nickel desulfurization of the ethylene dithioketal of **7** gave bicyclo[3.3.1]-nonane. These show that the carbon skeleton is once again bicyclo[3.3.1]nonane, and the second reaction suggests that reductive dechlorination should be possible. This proved correct, since, when **7** was treated with a large excess of W-2 Raney nickel, 2-bicyclo[3.3.1]nonanol was obtained as an equilibrium mixture[17] of the two epimers.

The position of the chlorine relative to the carbonyl group was established by dehydrohalogenation to 6-bicyclo[3.3.1]nonen-2-one (**8**), a ketone previously isolated by Rogers.[18] Since the nmr spectrum of **8** shows no deflection of the base line at 2.5–3.0 ppm, we can state that the dehydrohalogenation product must contain less than 5% **3**. Thus the position of the chlorine at C_6 is clearly established, but its orientation is uncertain. Allinger and Liang[19] have shown that the orientation of a chlorine on a cyclohexane ring can be deduced from the position of the C–Cl stretch in the infrared. Thus ν_{C-Cl} for axial chlorine should be 661–678 cm^{-1} and ν_{C-Cl} for equatorial chlorine should be 749–758 cm^{-1}. Ketone **7** has two bands, one at 768 cm^{-1} and a second of lesser intensity at 715 cm^{-1}. These suggest that **7** is a mixture of epimers.

Migration of a chlorine during internal acylation is not without precedent. Nenitzescu and coworkers[20] have studied this phenomenon with some care, and have shown that the main product normally obtained has the chlorine atom on that carbon atom most distant from the carbonyl group which permits formation of a secondary chloride. Our results agree with this generalization. That the chlorine migration can indeed occur under the conditions of the reaction was confirmed by treating **4** with aluminum chloride in dichloroethane. A good yield of **7** was obtained.

Synthesis of 2-Bicyclo[3.3.1]nonanone (6).—Since the occurrence of hydride transfers in carbonium ion reactions and particularly in Friedel–Crafts reactions[21] is well established, it seemed that the use of an ap-

(16) J. P. Schaefer, J. C. Lark, C. A. Flegal, and L. M. Honig, *J. Org. Chem.*, **32**, 1372 (1967).

(17) E. N. Marvell and R. S. Knutson *ibid.* **35**, 388 (1970); K. H. Baggeley, J. R. Dixon, J. M. Evans, and S. H. Graham, *Tetrahedron*, **23**, 299 (1967).

(18) We are indebted to Professor N. A. J. Rogers of the University of Lancaster for spectral data.

(19) N. L. Allinger and C. D. Liang, *J. Org. Chem.*, **32**, 2391 (1967).

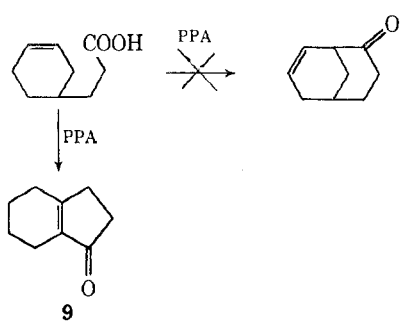
(20) C. D. Nenitzescu and I. Gavat, *Ann. Chim.* (Paris), **519**, 260 (1935); C. D. Nenitzescu, I. Gavat, and K. Cocora, *Chem. Ber.*, **73**, 233 (1940); C. D. Nenitzescu and A. M. Glatz, *Bull. Soc. Chim. Fr.* 218 (1961).

(21) C. D. Nenitzescu, *Chem. Ber.*, **69**, 1820 (1963).

propriate solvent might permit synthesis of **6**. This aim was realized when a hydrocarbon solvent was employed. Studies with pentane, 3-methylpentane, cyclohexane, and methylcyclohexane at temperatures ranging from 0° to solvent reflux showed that the use of cyclohexane at reflux was most effective. The main by-product was isolated by preparative glpc and spectral examination showed that it was a hydrocarbon. Presumably, it is derived from the solvent carbonium ion formed in the hydride-transfer process, but it was not examined further. Since this hydrocarbon is easily separated from the desired **6** by column chromatography, this route constitutes a very economical synthesis for **6** from 4-vinylcyclohexene in three steps with an overall yield of *ca.* 20%.

Synthesis of 8-Chlorobicyclo[3.3.1]nonan-2-one (4).—As the data of Table I suggest, the most effective conditions for the preparation of **4** involve the use of titanium tetrachloride in 1,2-dichloroethane. Isolation of **4** from the product mixture was most conveniently accomplished by distillation followed by low-temperature crystallization. Despite the inefficiency of this process, yields of *ca.* 30% pure **4** can be obtained routinely.

Cyclization of 1 in Polyphosphoric Acid.—Finally, an attempt to simplify the synthesis of **3** was made by treating 3-(3-cyclohexen-1-yl)propionic acid with polyphosphoric acid (PPA). No **3** was formed in this



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process, which gave an excellent yield of 2,3,4,5,6,7-hexahydro-1-indenone (**9**). Presumably, a shift of the double bond precedes the ring-closure step. Thus by appropriate control of catalyst, solvent, and substrate, this general synthetic route can be used to convert 4-vinylcyclohexene into **3**, **4**, **6**, **7**, or **9** in reasonable yields by a process involving no more than three steps in any case.

Experimental Section

Diethyl 2-(3-Cyclohexen-1-yl)ethane-1,1-dicarboxylate.—A tosylate was prepared in 96% yield from 485 g (4.34 mol) of 3-cyclohexen-1-ylmethanol[9] according to the method of Tipson.[22] The crude tosylate, ir (neat) 1590, 1500, 1350, and 1180 cm^{-1}, was used directly in the second step. To a solution containing 0.61 mol of sodium diethyl malonate in 450 ml of anhydrous ethanol was added over a 5-hr period 154 g (0.60 mol of crude tosylate). The reaction mixture was heated under reflux for 36 hr. To this was added 250 ml of water, and most of the ethanol was removed under reduced pressure. The residue was acidified with dilute hydrochloric acid. The organic layer was separated and the aqueous layer was extracted with ether. The desired product was isolated by fractional distillation: bp 95–99° (2 mm); yield 102.6 g (70%); $n^{20}D$ 1.4620; ir 1740, 1650, 1465 1095, and 1055 cm^{-1}.

(22) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

Anal. Calcd for $C_{14}H_{22}O_4$: C, 66.12; H, 8.72. Found: C, 66.10; H, 8.62.

3-(3-Cyclohexen-1-yl)propionic Acid (1). Method A.—This method constitutes a modification of the method of Finkbeiner and Cooper.[12] A solution of *n*-propylmagnesium bromide in 775 ml of tetrahydrofuran was prepared from 32.1 g (1.32 g-atoms) of magnesium and 147.8 g (1.20 mol) of *n*-propyl bromide under a nitrogen atmosphere. To this was added slowly 2.9 ml of titanium tetrachloride, and, after the vigorous reaction had subsided, 108 g (1.00 mol) of 4-vinylcyclohexene was added. The reaction mixture was heated under reflux for 16 hr. After 100 ml of diethyl ether had been added, the solution was cooled to −5° and carbon dioxide was passed over the stirred solution at a rate which permitted maintenance of the reaction mixture below 10°.

The solution was treated with a slurry of 550 ml of 10% sulfuric acid and ice chips. The aqueous layer was extracted with ether, and the combined organic layers were extracted with 20% sodium hydroxide. Careful neutralization of the cold, basic solution with concentrated hydrochloric acid gave an oil: bp 89–90° (0.05 mm); yield 76 g (49%); mp 33–35° (lit.[12] mp 31–32°).

Method B.—A mixture of 101 g (0.40 mol) of diethyl 2-(3-cyclohexen-1-yl)ethane-1,1-dicarboxylate and 750 ml of 10% aqueous potassium hydroxide was stirred at room temperature until the organic layer had dissolved. The mixture was washed with ethyl ether and acidified with dilute sulfuric acid. The acidic solution was extracted several times with ether. Evaporation of the ether gave 2-(3-cyclohexen-1-yl)ethane-1,1-dicarboxylic acid, mp 120–121° after recrystallization from benzene.

Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.86; H, 7.10.

The above acid (74.5 g, 0.376 mol) was heated in 800 ml of xylene at 132° for 16 hr. The xylene was removed by distillation and the residue was distilled, bp 87–88° (0.2 mm), to give 55.3 g (95%) of 3-(3-cyclohexen-1-yl)propionic acid, mp 34.5–36°.

Method C.—To 29.8 g (0.212 mol) of 3-(3-cyclohexen-1-yl)-propanol[9] in 1500 ml of acetone at 0° was added dropwise *ca.* 120 ml of a solution containing 32.0 g of chromium trioxide and 27.6 ml of sulfuric acid. As soon as the red color of the reagent persisted for a few minutes, the reaction mixture was allowed to stand overnight. About 500 ml of water was added and the acetone was removed under reduced pressure. The organic product was taken up in ether and was isolated by distillation: bp 81–82° (0.6 mm); mp 33–35°; yield 25.9 g (79%).

3-(3-Cyclohexen-1-yl)propionyl Chloride (2).—This acid chloride was prepared from the above acid by treatment with oxalyl chloride as described earlier.[5d] The crude product was used in the Friedel–Crafts step without further purification. The preparation of **2** was also carried out in larger scale, as described below.

A solution containing 120 g (0.78 mol) of 3-(3-cyclohexen-1-yl)-propionic acid and 69 g of pyridine in 1200 ml of dry benzene was cooled to 5°. Purified thionyl chloride (190 g, 1.6 mol) was added dropwise and the reaction mixture was stirred for 6 hr at 0–5° and 2 hr at 5–15°. Excess thionyl chloride and the benzene were removed under reduced pressure and the product was isolated by distillation, bp 58–60° (0.5 mm), yield 115 g (86%). This product was used without further purification.

7-Bicyclo[3.3.1]nonen-2-one (3).—The ketone **3** was prepared in 55% yield according to the procedure described earlier:[5d] nmr (CCl_4) δ *ca.* 6.0 and 5.8 (modified AB, $J_{AB} \cong 9$, $J_{AX} \cong 3$ Hz, 2 H), 2.82 (m, 1 H), and 2.6–1.7 (br m, 9 H).

8-Chlorobicyclo[3.3.1]nonan-2-one (4). Method A.—The still residues obtained after the isolation of **3** as described above contain by glpc analysis (190°, Ucon Polar column) mainly a mixture of **4** and **5**. These could be separated readily by chromatography on activity II alumina, **3** being eluted with 10–20% benzene–pentane and **4** by 80–100% benzene–pentane as a white, crystalline material: mp 40–46°; ir 1710, 750, and 684 cm^{-1}; nmr (CCl_4) δ 4.4 (br s, 1 H) and 2.6–1.5 (br m, 12 H).

Anal. Calcd for $C_9H_{13}OCl$: C, 62.61; H, 7.59. Found: C, 62.80; H, 7.55.

Method B.—To a solution containing 10 g (0.058 mol) of **1** in 500 ml of 1,2-dichloroethane was added dropwise 25 g (0.13 mol) of titanium tetrachloride. After the addition had been completed, the solution was stirred for 6 hr at 25°. A slurry of ice chips in 500 ml of 10% hydrochloric acid was added, and the layers were separated. The aqueous layer was extracted with methylene chloride, and the combined organic layers were dried (Na_2SO_4). After the solvent had been removed, the product was

distilled through a short column packed with glass helices, bp *ca.* 60–80° (0.8 mm), yield 4.2 g (38%). Glpc analysis (1/4 in. × 5 ft SF-96 on Chromosorb at 150°) showed that this fraction contained *ca.* 90% **4**. Further purification was achieved by fractional freezing. A product, mp 40–46°, was obtained (28%).

6-Chlorobicyclo[3.3.1]nonan-2-one (7).—A mixture containing 10.1 g (0.059 mol) of **2** and 17.2 g (0.129 mol) of aluminum chloride in 240 ml of 1,2-dichloroethane was stirred for 5 hr at 25°. The mixture was cooled in an ice bath and 120 ml of 10% hydrochloric acid was added. The aqueous layer was extracted with dichloroethane, and the combined organic layers were washed with sodium bicarbonate and water. The solution was dried ($MgSO_4$) and the solvent was removed *in vacuo*. After removal of a small amount of liquid material (2.0 g), the product was isolated from the tarry residue by vacuum sublimation, bp 165° (bath temperature, 0.05 mm). The product was purified by resublimation, giving 4.12 g (41%) of **7**: mp 78–81°; ir (CS_2) 1710, 986, 768, and 715 cm^{-1}; nmr (CCl_4) δ 4.28 (br s, 1 H) and 2.6–1.4 (m, 12 H).

Anal. Calcd for $C_9H_{13}OCl$: C, 62.61; H, 7.54; Cl, 20.57. Found: C, 62.54; H, 7.62; Cl, 20.42.

A semicarbazone derivative prepared according to the procedure of Cheronis and Entrikin[23] melted at 184–185°.

Anal. Calcd for $C_{10}H_{16}N_3OCl$: C, 52.29; H, 6.97. Found: C, 52.06; H, 6.98.

2-Bicyclo[3.3.1]nonanone (6).—A solution of 10.0 g (0.056 mol) of **2** in 150 ml of cyclohexane was added dropwise to a rapidly stirred suspension of 15.5 g (0.116 mol) of aluminum chloride in 1 l. of boiling cyclohexane. After addition was complete, the mixture was stirred for 15 min and cooled in an ice bath. *Ca.* 300 ml of dilute hydrochloric acid was added and the organic layer was separated, washed with saturated sodium sulfate, and dried ($MgSO_4$). The solvent was removed by distillation using a Vigreux column, and the product was isolated by distillation, bp 34–38° (0.02 mm). The solid which collected in the head was washed out with pentane and purified by sublimation, mp 127–130° (capillary) (lit.[14] mp 134–137°), yield 1.41 g.

The distillate was analyzed by glpc (15 ft × 0.125 in. 5% SE-30 on Chromosorb G column at 150°) and was found to contain two impurities which eluted before the ketone. Isolation of the impurities by preparative glpc (14 ft × 0.375 in. 20% SF-96 on firebrick column at 130°) and examination of their nmr spectra showed only aliphatic hydrogen.

For synthetic runs the distillate was chromatographed over activity II alumina. The impurities eluted in the first fractions with hexane as eluent and the desired ketone was eluted after these, mp 128–130° (capillary), yield 2.32 g. The overall yield was 3.73 g (46%).

2,3,4,5,6,7-Hexahydro-1-indenone (9).—A mixture of 4.07 g (0.026 mol) of 3-(3-cyclohexen-1-yl)propionic acid and 59 g of polyphosphoric acid was heated on a steam bath for 2.5 hr. The reaction mixture was shaken at regular intervals during this time. The cooled mixture was diluted to 200 ml with water, and this solution was extracted with ether. The ether extracts were washed with water, dried ($MgSO_4$), and concentrated *in vacuo*. Distillation, bp *ca.* 70° (0.4 mm), gave 2.66 g (74%) of ketone, λ_{max} 238 nm (log ϵ 4.10) [lit.[24] λ_{max} 236 nm (log ϵ 4.09)]. The 2,4-dinitrophenylhydrazone derivative melted at 237–238° (lit.[24] mp 238–239°).

6-Bicyclo[3.3.1]nonen-2-one (8). Method A.—A mixture of 500 mg (2.9 mmol) of **7**, 16 ml of benzene, 5 ml of ethylene glycol, and 19 mg of *p*-toluenesulfonic acid was heated under reflux for 5.5 hr. Water was removed from the reaction mixture *via* a Dean–Stark separator. The reaction mixture was washed with 10 ml of 1% sodium hydroxide, and the aqueous layer was extracted with ether. The combined benzene and ether solutions were washed with water, and distilled until the head temperature reached 80°. The residue (5 ml) showed no carbonyl or enol ether bands in the infrared.

This residue was added to a solution containing 29 mmol of sodium glycolate in 20 ml of ethylene glycol, and the reaction mixture was heated at 155° for 4 hr. The cooled solution was acidified with 10% sulfuric acid and extracted with pentane. Most of the pentane was distilled from this solution and the residue was heated under reflux with 10 ml of acetone and 7 ml of 4% sulfuric acid for 1 hr. The solution was diluted with water and extracted with pentane. The main component of this solution was isolated by preparative glpc (5 ft × 0.25 in. 20% SF-96 column at 135°): mp 61.5–62.5°; yield 134 mg (34%); ir (CCl_4) 3050, 1710, and 1105 cm^{-1}; nmr (CCl_4) δ 5.84 (d, 2 H, J = 3 Hz) and 2.65–1.6 (m, 10 H); λ_{max} (CH_3OH) 293 nm (ϵ 41).

A semicarbazone derivative prepared according to the procedure of Cheronis and Entrikin[23] melted at 191–192°.

Anal. Calcd for $C_{10}H_{15}N_3O$: C, 62.12; H, 7.82. Found: C, 61.98; H, 7.69.

Method B.—Ketone **7** (200 mg, 1.16 mmol) was stirred for 36 hr with a solution of 506 mg (2.32 mmol) of silver trifluoroacetate in 10 ml of trifluoroacetic acid. The precipitate was removed by filtration, and the filtrate was diluted with water and extracted with pentane. The pentane solution was washed free of acid and concentrated *in vacuo*. Examination of the concentrate by glpc (SF-96 column at 160°) showed that the reaction had not proceeded to completion (60% from glpc). The product was isolated by preparative glpc as above, giving 42 mg (27% or 45% based on amount of **7** consumed) of material, mp 61–62°.

Hydrogenation of 3.—A sample of **3** was hydrogenated in methanol solution over palladium on charcoal. The catalyst was removed by filtration and the product was isolated by preparative glpc. The nmr and mass spectra of the compound were identical with those of an authentic sample of **6**.

2-Bicyclo[3.3.1]nonene from 7.—A sample of **7** (250 mg, 1.45 mmol) was mixed with 146 mg (3.01 mmol) of hydrazine hydrate and 240 mg of potassium hydroxide in 2.5 ml of diethylene glycol. The solution was placed in a 10-ml flask fitted with a cold-finger condenser, and was heated at 50° for 4 hr and then at 200° for 4 hr. The solid which collected on the condenser was purified by preparative glpc (5 ft × 0.25 in. 20% SF-96 column at 100°), mp 99–100° (lit.[16] mp 96.5–97°), yield 80 mg (32%).

Bicyclo[3.3.1]nonane from 7.—A solution of 500 mg (2.9 mmol) of **7** in a small amount of anhydrous ether was combined with 0.5 ml of ethanedithiol and 8 drops of boron trifluoride ethereate. The mixture was allowed to stand at room temperature for 2 hr, after which the excess ethanedithiol was removed by azeotropic distillation with absolute ethanol. The residue was diluted with 5 ml of absolute ethanol and heated at reflux for 10 hr over 5.5 g of W-2 Raney nickel.

The catalyst was removed by filtration, and the filtrate was diluted with water and then extracted with pentane. The product was isolated by glpc, mp 143–145° (lit.[16] mp 143–144°), yield 102 mg (28%).

2-Bicyclo[3.3.1]nonanol from 7.—A solution of 311 mg (1.81 mmol) of **7** in 5 ml of methanol was stirred at reflux with 3 g of W-2 Raney nickel for 10 hr. The catalyst was removed by filtration and extracted in a Soxhlet apparatus with methanol. The combined methanol solutions were diluted with water and extracted with pentane. Evaporation of the pentane gave 147 mg (47%) of 2-bicyclo[3.3.1]nonanol. Purification by preparaglpc (5 ft × 0.25 in. 20% SF-96 column at 145°) gave a sample, mp 178–182° (lit.[16] mp 177–178° for *endo*-2-ol and 176–177° for *exo*-2-ol). Glpc comparison with authentic samples showed this material to contain *ca.* 70% *endo*-2-ol and 30% *exo*-2-ol.

Reduction of 4.—Crude product from the stannic chloride catalyzed reaction of **2** containing *ca.* 40% **3**, 30% **4**, and 20% **5** (glpc analysis) was hydrogenated over palladium on charcoal in methanolic potassium hydroxide (10%) until no further hydrogen was absorbed. The catalyst was removed and the solution was neutralized with dilute hydrochloric acid. Water was added and the solution was extracted with pentane. After removal of the pentane, the residue was purified by sublimation. Analysis by glpc (SF-96 column at 150°) showed that **3** and **4** had disappeared and a new product with the same retention time as **6** (internal comparison) had appeared. However, **5** remained unaltered. The mass spectrum of the reduction product was identical with that of an authentic sample of **6**.

Dehydrohalogenation of 4. Method A.—A sample (400 mg, 2.35 mmol) of **4** was treated with 1.0 g of silver trifluoroacetate as described under the dehydrohalogenation of **7**. The product gave one peak on glpc analysis (5 ft × 0.25 in. SF-96 column): ir 3025, 1755, 1710, and 1645 cm^{-1}; λ_{max} 297 nm (ϵ *ca.* 100); nmr (CCl_4) δ 5.8 (m, 2 H) and unresolved multiplets at 3.1, 2.8, and 0.9–2.7.

Method B.—Ketone **4** (200 mg, 1.18 mmol) and 400 mg of silver nitrate were mixed in 30 ml of 95% ethanol. The mixture was boiled for 8 hr, and after the solution had been diluted with water, the product was taken up in pentane. The product was collected from glpc and had spectral properties in full agreement

(23) N. D. Cheronis and J. B. Entrikin, "Identification of Organic Compounds," Interscience Publishers, Inc., New York, N. Y., 1963, p 320.

(24) R. L. Frank and R. C. Pierle, *J. Amer. Chem. Soc.*, **73**, 724 (1951).

with those noted above. The intensities of the 1755- and 1710-cm^{-1} bands were approximately equal.

Registry No.—**2**, 22482-52-6; **3**, 16957-72-5; **4**, 22482-54-8; **6**, 2568-17-4; **7**, 22482-56-0; **7** semicarbazone, 22482-57-1; **8**, 22482-58-2; **8** semicarbazone, 22482-59-3; diethyl 2-(3-cyclohexen-1-yl)ethane-1,1-dicarboxylate, 22482-60-6; 2-(3-cyclohexen-1-yl)ethane-1,1-dicarboxylic acid, 22482-61-7; 3-(3-cyclohexen-1-yl)propionic acid, 22482-62-8.

Transannular Reactions during Solvolyses of *exo*-2,3-Epoxybicyclo[3.3.1]nonane[1]

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Solvolysis of *exo*-2,3-epoxybicyclo[3.3.1]nonane (**1**) at 0° in trifluoroacetic acid gave (50–60%) a mixture of 7-bicyclo[3.3.1]nonen-*exo*-2-ol (**3**) and 6-bicyclo[3.3.1]nonen-*exo*-2-ol (**4**). Acetolysis of **1** gave (95%) a mixture containing 53% diols and 47% enols. Glpc analysis of the total mixture showed 46% *exo*-2-*endo*-3-bicyclo[3.3.1]-nonadiol (**9**), 23% a mixture of **3** and **4**, 21% 3-bicyclo[3.3.1]nonen-*exo*-2-ol (**7**), 5% *exo*-2-*exo*-7-bicyclo-[3.3.1]nonadiol (**10**), 3% a compound tentatively identified as 7-bicyclo[3.3.1]nonen-*exo*-3-ol (**8**), and 2% a diol tentatively assigned the structure *endo*-2-*exo*-3-bicyclo[3.3.1]nonadiol (**11**). The results are compared with similar solvolyses of *cis*-cyclooctene oxide.

In 1944 the classic and elegant experiments of Bartlett, Condon, and Schneider[3] showed that hydride transfer from a nonactivated CH group to a carbonium ion can occur with great rapidity. With the exception of such special reactions as 1,2-hydride shifts and cases where the product of reaction with the solvent regenerates the carbonium ion,[4] this hydride shift was not found to compete successfully with reaction between the carbonium ion and a nucleophilic solvent. Thus the discovery that a transannular hydride shift will compete quite effectively with a nucleophilic solvent for the carbonium ions of medium rings[5] evoked considerable interest. Despite a great deal of effort by a number of investigators,[6] the relative importance of such factors as proximity of the CH group to the cation, strain in the ring, and hindrance to reaction with the solvent is not yet clear, and questions of whether sequential ion formation, rearrangement, and solvent reaction is required or whether partial or fully concerted processes are possible have not been unequivocally answered. The conformational mobility of the medium rings has served to complex the investigative problem and has prevented a better understanding of the role which conformation must play in the transannular hydride transfer.

Hoping to be able to answer some of these questions about transannular processes, we began a comprehensive study of the chemistry of medium rings conformationally restricted by bridging. Our first efforts were directed at the symmetrically bridged cyclooctane ring, *viz.*, bicyclo[3.3.1]nonane. For molecules having only hydrogen on the *endo* sides of carbons 3 and 7, this ring is known[7] to have a double-chair conformation. Thus it should provide an ideal substrate for study of the mechanistic details of transannular processes. The present paper reports a comparison of the behavior of *exo*-2,3-epoxybicyclo[3.3.1]nonane (**1**) with that of *cis*-cyclooctene oxide[8] under comparable conditions.[9]

Solvolyses and Product Identification.—Epoxidation of 2-bicyclo[3.3.1]nonene was carried out by the method of Payne.[10] The product was shown to be *exo*-2,3-epoxybicyclo[3.3.1]nonane (**1**) by reduction to the known *exo*-2-bicyclo[3.3.1]nonanol (**2**).[11] Solvolysis of **1** was performed first in trifluoroacetic acid, and a modest yield (50–60%) of monomeric product was recovered after hydrolysis with dilute base. The crude product was purified chromatographically and a crystalline enol was recovered. This enol was reduced to **2**, which shows that ring opening occurred without loss of configuration at C_2.

Based on the assumption that this enol must be derived from a C_7 carbonium ion, a mixture of 7-bicyclo[3.3.1]nonen-*exo*-2-ol (**3**) and 6-bicyclo[3.3.1]nonen-*exo*-2-ol (**4**) is expected. However, we were unable to separate the product either by glpc or thin layer chromatography. Therefore, the enol fraction was oxidized by Jones oxidant. It is assumed that under these conditions the position of the double bond is not altered, since this procedure is known to leave even sensitive β,γ double bonds unaltered.[12] The oxidation product, mp 55–68°, was again inseparable on thin layer chromatography or glpc. Both 7-bicyclo[3.3.1]-nonen-2-one (**5**)[13] and 6-bicyclo[3.3.1]nonen-2-one (**6**)[14] were synthesized, and known mixtures of the two

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