clo[2.1.1]hexene,[9] and various other compounds containing cyclobutane ring, the C···C distance between the bridgehead atoms is the shortest nonbonded distance on record. If C_1 and C_3 are assumed to be nearly sp^2 hybridized, the almost p_z orbital of C_1 can participate in bonding with H_6, while its back lobe can overlap with the p_z from C_3. This type of hybridization at the bridgehead carbons does account for the large long-range proton spin–spin coupling constant (J_{C-H} = 18 cps) reported by Wiberg, *et al.*[5] This assumption is also supported by the product distribution found in the chlorination of bicyclo[1.1.1]pentane with *t*-butyl hypochlorite. This reaction produces 45% of 1-chlorobicyclo[1.1.1]pentane[5] and only 2% of 2-chlorobicyclo-[1.1.1]pentane, while the rest is the unreacted compound. This contrasts with bicyclo[2.2.1]heptane which is inert to 1 substitution.[10] The unexpectedly small ∠CCC at the methylenes is thus rationalized. A comparison of the environment at the bridgehead carbons in bicyclo[1.1.1]pentane, bicyclo[2.1.1]hexane, and bicyclo[2.2.1]heptane is postponed until the structure of bicyclo[2.1.1] has been redetermined.

The nonbonded $H_9 \cdots H_{10}$ distance is 2.45 Å, which is approximately twice the van der Waals radius of hydrogen atoms. This separation is consistent with the coplanarity of the H atoms with the methylene carbons, since no significant stabilization would be achieved by an out-of-plane distortion. The surprising feature is the small ∠HCH (104°). Clearly, the hybridization around the methylene carbons is not well approximated by an sp^3 combination. Perhaps the simplest description is to assume that the lobes of their relatively unhybridized p orbitals extend toward the bridgehead carbons and utilize principally the s orbitals for bonding with the hydrogen atoms. The results of an SCF-MO calculation of overlap populations and comments on this structure will shortly be submitted for publication by J. F. C.

(9) Joseph F. Chiang and S. H. Bauer, to be published.
(10) E. C. Kooyman and G. V. Vegter, *Tetrahedron*, 4, 382 (1958).

Acknowledgments. The authors thank Mr. R. Hilderbrandt for taking the electron-diffraction photographs, and Dr. F. Uno and Professor J. Meinwald for the sample. We are grateful to Mr. J. Higgins of the Computer Center at SUNY, Binghamton, for various help during the analysis and State University College at Oneonta for furnishing the computer time.

Appendix A. Coordinates of Bicyclo[1.1.1]pentane[a]

	x	*y*	*z*
C_1	0	0	0.9222
C_2	1.2395	0	0
C_3	0	0	−0.9222
C_4	−0.6198	1.0734	0
C_5	−0.6198	−1.0734	0
H_6	0	0	2.0222
H_7	0	0	−2.0222
H_8	1.9175	−0.8662	0
H_9	1.9175	0.8662	0
H_{10}	−0.2086	2.0937	0
H_{11}	−1.7089	1.2275	0
H_{12}	−1.7089	−1.2275	0
H_{13}	−0.2086	−2.0937	0

[a] For numbering system, see Figure 4.

1-Methylbicyclo[3.1.1]heptan-6-one and Related Substances

Ernest Wenkert, Peter Bakuzis, Ronald J. Baumgarten, David Doddrell, P. W. Jeffs, Curtis L. Leicht, Richard A. Mueller, and A. Yoshikoshi

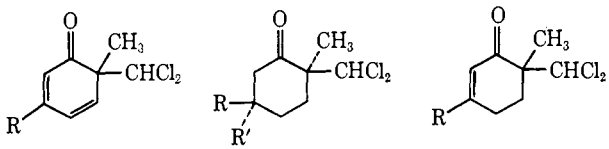
Contribution from the Department of Chemistry, Indiana University, Bloomington, Indiana 47401. *Received July 17, 1969*

Abstract: Base-induced conversions of 2-methyl-2-dichloromethylcyclohexanones to derivatives of the title compound and elucidation of their stereochemistry are discussed. Benzene solvent shifts of proton magnetic resonance spectra of haloolefins and their stereochemically diagnostic value are introduced. Syntheses of sesquiterpene models based on the bicyclo[3.1.1]heptane system are portrayed.

The polyfunctionality of alkyldichloromethylcyclohexadienones, products of alkali-induced interaction of alkylphenols with chloroform, makes these substances attractive starting materials for the synthesis of complex systems but necessitates prior investigations of their general chemical behavior. Such studies recently led to the discovery of facile transformations of 4-methyl-4-dichloromethyl-2,5-cyclohexadienone into polyfunctional bicyclo[3.3.1]nonanes and *cis*-decalins[1] and to the exploitation of the benz analog in the synthesis of tricarbocyclic diterpenes.[2] As further expansion of this fruitful area of research the chemical conduct of 6-methyl-6-dichloromethyl-2,4-cyclohexadienone (**1a**), a product of the Reimer–Tiemann reaction of *o*-cresol,[3] was examined.

Standard hydrogenation of **1a** has yielded 2-methyl-2-dichloromethylcyclohexanone (**2a**).[4] Controlled palladium-catalyzed hydrogenation and cessation of the reaction after a *ca.* 1-mole uptake of hydrogen yielded preponderantly the conjugated ketone **3a** and some of its isomer **4**. With time or on sulfuric acid treatment

(1) E. Wenkert, F. Haviv, and A. Zeitlin, *J. Am. Chem. Soc.*, **91**, 2299 (1969).
(2) (a) E. Wenkert and T. E. Stevens, *ibid.*, **78**, 5627 (1956); (b) E. Wenkert, A. Afonso, J. B-son Bredenberg, C. Kaneko, and A. Tahara, *ibid.*, **86**, 2038 (1964).
(3) K. Auwers and F. Winternitz, *Ber.*, **35**, 465 (1902); K. Auwers and G. Keil, *ibid.*, **35**, 4207 (1902).
(4) K. von Auwers and E. Lange, *Ann.*, **401**, 317 (1913).

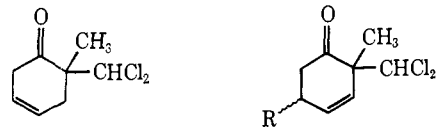


1a, R = H
b, R = *i*-Pr

2a, R = R′ = H
b, R = *i*-Pr; R′ = H
c, R = H; R′ = *i*-Pr

3a, R = H
b, R = *i*-Pr

the latter reverted to the former product. Reduction of the dienone **1a** with sodium borohydride in ethanol followed by Jones oxidation of the resultant hydroxyolefin led to the third olefinic ketone (**5a**).



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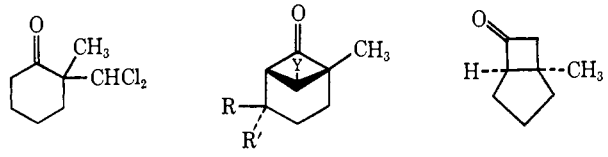
5a, R = H
b, R = *i*-Pr

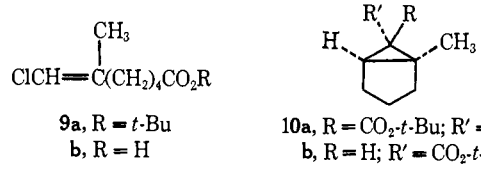
Tri-*n*-butyltin hydride reduction[5] of the cyclohexanone **2a** produced the monochloro compound **6**,[6] whose treatment with potassium *t*-butoxide yielded the cyclobutanone **7a**,[7] a trace of another cyclobutanone (**8**),[7] and unidentified dimeric products. Similar exposure of **2a** to base led to the previously reported[8] chlorocyclobutanone **7b**, accompanied by *t*-butyl 6-methyl-7-chloro-6-heptenoate (**9a**) and traces of esters **10a** and **10b**. The acyclic ester was identified by its hydrolysis to the known acid **9b**[9] and the bicyclic esters by spectral comparison with their methyl ester equivalents.[10,11] Tri-*n*-butyltin hydride reduction of **7b** gave **7a**.



6

7a, R = R′ = Y = H
b, R = R′ = H; Y = Cl
c, R = *i*-Pr; R′ = H; Y = Cl
d, R = H; R′ = *i*-Pr; Y = Cl

8



9a, R = *t*-Bu
b, R = H

10a, R = CO_2-*t*-Bu; R′ = H
b, R = H; R′ = CO_2-*t*-Bu

The transformation of ketone **2a** into ester **9a** can be envisaged to proceed by way of a carbonyl–solvent addition intermediate[9] whose fragmentation is representative of the frequently encountered 1,3-elimination reactions.[12,13] In view of the exclusive formation of one geometric isomer of the chloroolefin **9a**, the stereochemical details of the fragmentation need to be considered. If it be assumed that the fragmenting species possesses a chairlike cyclohexane ring and an equatorial dichloromethyl group, the cleaving carbon–chlorine and carbon–carbon bonds are aligned in a *trans* (coplanar) manner and the remaining chlorine is oriented in such a direction as to minimize nonbonded interactions and dipole repulsions (*cf.* **11**), the product would be expected to have the stereochemistry depicted in **12a**.[14] A similar analysis of the recently reported conversion of ketol **13** into phenol **14**[1] (stereochemistry heretofore not indicated) leads to the assignment of the same configuration of the chloropropenyl group of **14** as that of **12a**.

While no chemical experiments were devoted to the stereochemistry problem, one solution thereof presented itself in the realm of solvent shifts of the pmr spectra of the chloroolefins **12a** and **12b**, the product of O-methylation of phenol **14**.[15] If it be supposed that solute–solvent complexes of benzene solutions of haloolefins mainly responsible for the differences of

(5) H. G. Kuivila in F.G.A. Stone and R. West, *Advan. Organometal. Chem.*, 1, 47 (1964).

(6) C. R. Johnson, C. J. Cheer, and D. J. Goldsmith, *J. Org. Chem.*, 29, 3320 (1964).

(7) E. Wenkert and D. P. Strike, *ibid.*, 27, 1883 (1962); K. B. Wiberg and G. W. Klein, *Tetrahedron Lett.*, 1043 (1963); S. Julia and C. Gueremy, *Bull. Soc. Chim. Fr.*, 2994 (1965); F. Nerdel, D. Frank, and H. Marschall, *Chem. Ber.*, **100**, 720 (1967).

(8) R. M. Dodson, J. R. Lewis, Wm. P. Webb, E. Wenkert, and R. D. Youssefyeh, *J. Am. Chem. Soc.*, **83**, 938 (1961).

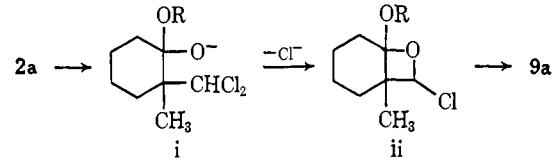
(9) M. G. Reinecke, *J. Org. Chem.*, **28**, 3574 (1963).

(10) E. Wenkert, P. Bakuzis, R. J. Baumgarten, and C. L. Leicht, manuscript in preparation.

(11) The mode of formation of the rearrangement products **8** and **10** will be discussed elsewhere.[10]

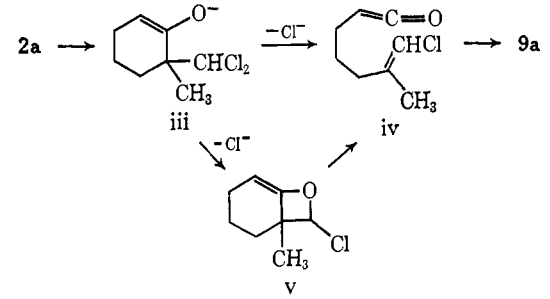
(12) *Cf.* E. Wenkert and Y. Gaoni, *J. Org. Chem.*, **31**, 3809 (1966), and references cited therein.

(13) Three alternate mechanisms may not be overlooked. One involves the solvent addition product i, intramolecular chloride displacement, and thermal fragmentation of the resultant oxetane ii. This reaction sequence is reminiscent of but not identical with the methoxide-induced conversion of α-arenesulfonyloxymethyl-α-ethylbutyraldehyde into 2-methoxy-3,3-diethyloxetane and 1-methoxy-2-ethyl-1-butene [J. Janculer, F. Nerdel, D. Frank, and G. Barth, *Chem. Ber.*, 100, 715 (1967)] and related reactions [F. Nerdel and H. Kressin,



i ii

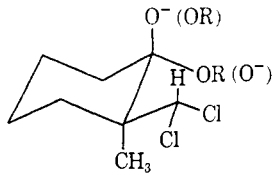
Ann., **707**, 1 (1967)]. The other two routes implicate enolate iii, the intermediate responsible for the creation of cyclobutanone **7b**, as primary way-station. One involves 1, 3 elimination to a ketene (iv) and solvent addition thereof, while the second includes a prior intramolecular chloride displacement and thermal decomposition of the highly strained oxetane v.



iii iv v

(14) This assignment is the reverse of that suggested for the olefinic acid **9b**, the product of hydroxide-induced fragmentation of **2a**.[9] However, the previous stereochemical analysis was based on the observation of spin–spin coupling ($J \approx 1.2$ cps) between the olefinic methyl and hydrogen substituents in the pmr spectrum of **9b** and the absence thereof in the reported spectrum of a related chloropropenyl compound and on the acceptance of a general $J_{cis} \geq J_{trans}$ relationship. Unfortunately this relationship is not universal [N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, p 108], *e.g.*, 2-chloro-2-butenes show J_{cis} = 1.2 cps and J_{trans} = 1.3 cps [R. G. Miller, T. J. Kealy, and A. L. Barney, *J. Am. Chem. Soc.*, **89**, 3756 (1967)]; 2-bromo-2-butenes show J_{cis} = 1.3–1.4 cps and J_{trans} = 1.4–1.5 cps [J. H. Richards and W. F. Beach, *J. Org. Chem.*, **26**, 623 (1961)]. Allylic coupling of geometric isomers is too similar to be of diagnostic value. (The chlorobutene **12e** reveals J_{cis} = 1.2 cps and J_{trans} = 1.0 cps.)

(15) The conversion of **14** into **12b** was carried out by Dr. A. Zeitlin.



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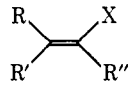
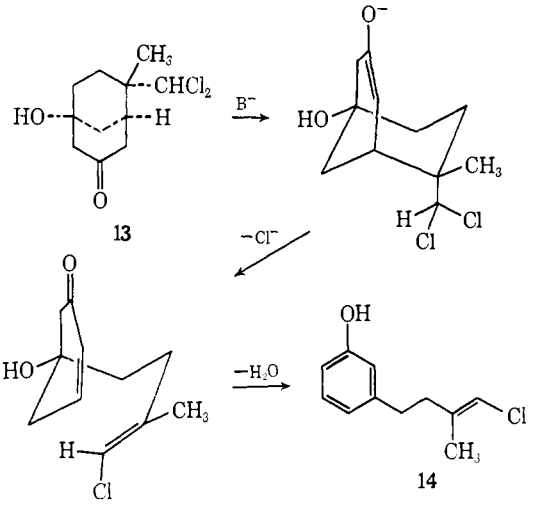
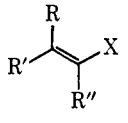


12a, R = Me; R′ = $(CH_2)_4CO_2$-*t*-Bu; R″ = H; X = Cl
b, R = Me; R′ = $(CH_2)_2C_6H_4$-*m*-OMe; R″ = H; X = Cl
c, R = R′ = H; R″ = Et; X = Br
d, R = Me; R′ = H; R″ = Et; X = Cl
e, R = R′ = Me; R″ = H; X = Cl



13 14

chemical shifts from those in innocuous solvents assume a configuration which places a benzene species at the positive end of and perpendicular to the haloolefin dipole (*cf.* **15**),[16,17] strong contrasts of the chemical shift differences of the two substituents β to the halogen (R and R′ groups) should appear. An early, little-used analysis of hydrogens directly attached to the double bond of a haloolefin confirm this conclusion: the chemical shift differences of benzene and neopentane solutions of vinyl bromide are 22.0 cps for the α-hydrogen (R″), 13.0 cps for the *cis*-β-hydrogen (R), and 25.5 cps for the *trans*-β-hydrogen.[18] Similarly, $\Delta\delta_{CDCl_3-C_6D_6}$ of the β-hydrogens of 2-bromo-1-butene (**12c**) are 0.35 and 0.17 ppm for the *trans* and *cis* components, respectively. A β-hydrogen *trans* to chlorine also is affected strongly; $\Delta\delta$ = 0.32 ppm for 3-chloro-2-pentene (**12d**).[19]



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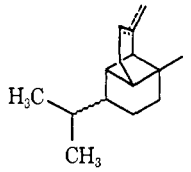


16

In accord with expectations the relationship of γ-hydrogens with the halogen also can be discerned from benzene solvent shifts. Thus, for example, the methyl groups of 1-chloro-2-methylpropene (**12e**) can be differentiated, the *trans* and *cis* substituents exhibiting $\Delta\delta$ values of 0.45 and 0.21, respectively. Similarly, the *cis*-methyl function of **12d** reveals a low $\Delta\delta$ value, 0.11. These facts allow assignment of the stereochemistry of the fragmentation products as depicted in **12a** and **12b**. Their olefinic methyl groups had $\Delta\delta$ values of 0.16 and 0.21, respectively, showing a *cis* relationship to the chlorine, while their *trans*-methylene groups exhibited $\Delta\delta$ values of 0.39 and 0.4, respectively. Thus the solvent shift data confirmed the stereochemistry derived by conformational analysis.

Table I. Chemical Shifts (ppm) of Olefinic Substituents of Compounds **12**

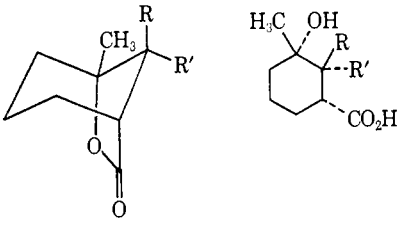
			α		*cis*-β		*trans*-β
12a	$CDCl_3$	H	5.77 (q)	CH_3	1.75 (d)	CH_2	2.07 (t)
	C_6D_6		5.57 (q)		1.59 (d)		1.68 (t)
	$\Delta\delta$		0.20		0.16		0.39
12b	$CDCl_3$	H	5.78 (m)	CH_3	1.83 (d)	CH_2	2.4 (m)
	C_6D_6		5.54 (m)		1.62 (d)		2.0 (m)
	$\Delta\delta$		0.24		0.21		0.4
12c	$CDCl_3$	CH_2	2.46 (q)	H	5.36 (m)	H	5.54 (m)
	C_6D_6		2.14 (q)		5.19 (m)		5.19 (m)
	$\Delta\delta$		0.32		0.17		0.35
12d	$CDCl_3$	CH_2	2.33 (q)	CH_3	1.69 (d of t)	H	5.48 (q)
	C_6D_6		2.12 (q)		1.58 (d)		5.16 (q)
	$\Delta\delta$		0.21		0.11		0.32
12e	$CDCl_3$	H	5.74 (m)	CH_3	1.78 (d)	CH_3	1.78 (d)
	C_6D_6		5.55 (m)		1.57 (d)		1.33 (d)
	$\Delta\delta$		0.19		0.21		0.45

Bicycloheptanone **7b** incorporates two of the three rings of the structurally intriguing sesquiterpenes **16**, the copaenes and ylangenes,[20] as well as functional groups situated properly for the possible introduction of the third ring. As a consequence a study of the stereochemistry of the bicycloheptanone, previously depicted without proof as in formula **7b**,[8] and of the synthesis and stereochemistry of its isopropyl derivatives was undertaken. The pmr spectrum of **7b** revealed a chloromethine singlet at 4.12 ppm and a bridgehead hydrogen triplet at 3.14 ppm (J = 3.8 cps) indicative of a *ca.* 90° dihedral angle between the vicinal methines and thus in conformity with the previous assignment of stereochemistry.[8] However, these data were considered insufficient and a full chemical structure proof deemed necessary in view of possible deviations of the Karplus relationship of coupling constants and dihedral angles of neighboring carbon–hydrogen bonds from normalcy in an environment of polar substituents and strained rings.[21]

Oxidation of **7b** with trifluoroperacetic acid yielded a lactone whose pmr spectrum—chloromethine singlet at 4.20 ppm, bridgehead hydrogen multiplet at 2.98 ppm, and methyl singlet at 1.53 ppm—was in agreement with structure **17a**. Alkaline hydrolysis of the lactone yielded chlorohydroxy acid **18a** and/or olefinic acid **19**.

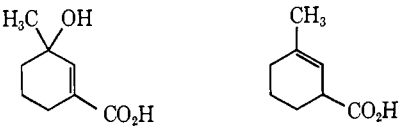
(16) T. Ledaal, *Tetrahedron Lett.*, 1683 (1968); D. Doddrell, unpublished observations; S. W. Tobey, *J. Org. Chem.*, **34**, 1281 (1969).
(17) E. T. Strom, B. S. Snowden, Jr., and P. A. Toldan, *Chem. Commun.*, 50 (1969), and references therein.
(18) W. G. Schneider, *J. Phys. Chem.*, **66**, 2653 (1962).
(19) This compound was donated kindly by Professor L. K. Montgomery.
(20) L. Westfelt, *Acta Chem. Scand.*, **21**, 152 (1967), and references therein; C. H. Heathcock, R. A. Badger, and J. W. Patterson, Jr., *J. Am. Chem. Soc.*, **89**, 4133 (1967).
(21) *Cf.* K. L. Williamson, *ibid.*, **85**, 516 (1963); M. Karplus, *ibid.*, **85**, 2870 (1963); K. L. Williamson, C. A. Lanford, and C. R. Nicholson, *ibid.*, **86**, 762 (1964).

Reduction of the latter with lithium in liquid ammonia produced 3-methyl-2-cyclohexenecarboxylic acid (**20**), whose treatment with hypochlorous acid afforded a chloro lactone. Since halolactonization is expected to proceed in a *trans* manner,[22] the new substance appeared to be the *trans*-chloro lactone **17b**. Its pmr spectrum—chloromethine broad doublet at 4.23 ppm (J = 5.0 cps), bridgehead hydrogen multiplet at 2.82 ppm, and methyl singlet at 1.45 ppm—and its conversion into chlorohydroxy acid **18b** and/or olefinic acid **19** on alkaline hydrolysis were in consonance with this assignment.[23] Furthermore, the nonidentity of this lactone with that derived from the bicycloheptanone confirmed the *cis*-chloro lactone relationship (**17a**) of the latter and a similar chlorine–carbonyl relationship **7b** in the bicyclic ketone.



17 **18**

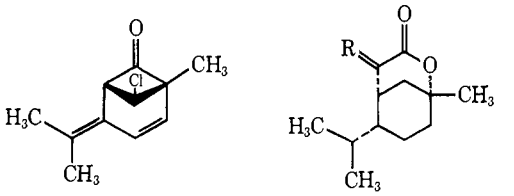
a, R = H; R′ = Cl
b, R = Cl; R′ = H



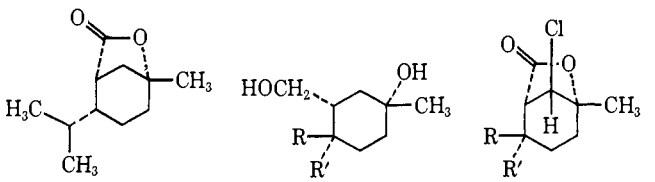
19 **20**

The bicycloheptanone had to possess a properly situated isopropyl group to be of use in a possible synthesis of the copaenes and ylangenes. As a consequence the preparation of the bicyclic substances **7c** and **7d** as well as their precursors **2b** and **2c**, respectively, came under investigation. In this connection an old study by Auwers was of relevance.[24] Auwers had carried out a reaction between cyclohexadienone **1a** and isopropylmagnesium bromide and had isomerized the resultant 1,4-addition product **5b** to the conjugated ketone **3b** by treatment with acid. These two reactions were reproducible and led the way to compounds **2b** and **2c**. Hydrogenation of **3b** yielded preponderantly cyclohexanone **2b**, whereas hydrogenation of **5b**, whose pmr spectrum showed it to be a mixture of two stereoisomers, afforded a 2:3 mixture of **2b** and **2c**. An alternate, fast route to these substances consisted of a Reimer–Tiemann reaction of carvacrol, followed by hydrogenation of the product (**1b**). This led preponderantly to **2b**.

On treatment of the two cyclohexanones, **2b** and **2c**, with potassium *t*-butoxide the bicyclic products **7c** and **7d**, respectively, were obtained. A direct, efficient method of synthesis of **7d** involved treatment of **1b** with sodium carbonate in dimethyl sulfoxide and hydrogenation of the resultant diene **21**. While pmr spectral analysis of **7c** and **7d** showed their chlorine substituents to have the same spatial relationship as the polar substituent of **7b**, little could be discerned regarding the stereochemistry of their isopropyl groups. Hence chemical correlation with a substance of known stereochemistry was desired and the diol **24a** chosen as the relay compound. Preparation of the latter followed a three-step reaction scheme: (a) condensation of lactone **22a** of established configuration[25] with ethyl formate, (b) ozonolysis of the hydroxymethylene lactone **22b** followed by oxidative work-up, and (c) lithium aluminum hydride reduction of the resultant γ-lactone **23**.

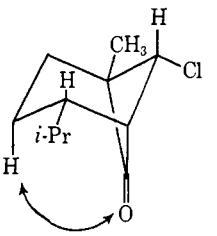


21 **22a**, R = H_2; **b**, R = CHOH



23 **24** **25**

a, R = H; R′ = *i*-Pr
b, R = *i*-Pr; R′ = H



26

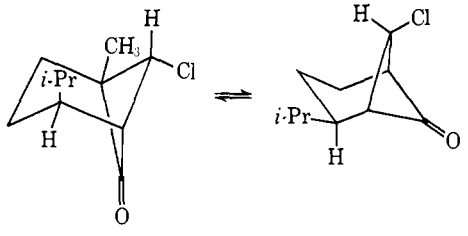
Oxidation of bicycloheptanone **7c** with *m*-chloroperbenzoic acid yielded lactone **25b**, while a similar treatment left ketone **7d** untouched. These facts, interpreted in terms of conformational analysis, constituted the first clue regarding the validity of the stereochemical assignments depicted in formulas **7c** and **7d**. While the carbonyl group of **7c** (conformations **27a**, **27b**, and nonchair forms between these extremes) is exposed to attack (especially form **27b**), the keto function of **7d** (conformation **26**) offers hindrance to peracid addition (see arrow in **26**). However, oxidation of the less reactive ketone (**7d**) with the powerful oxidizing agent trifluoroperactic acid led to the chloro lactone **25b**. Exhaustive lithium aluminum hydride reductions of the lactones **25a** and **25b** yielded diols **24a** and **24b**, respectively. The identity of diol **24a** with that derived from a substance of established stereochemistry confirmed the configurations of cyclohexanones **2b** and **2c** and all compounds derived therefrom.

(22) *Cf.* G. Berti, *Tetrahedron*, **4**, 393 (1958); Yu. A. Arbusov, V. T. Ivanor, M. N. Kolosov, Yu. A. Ovchinnikov, and M. M. Shemyakin, *Zh. Obshch. Khim.*, **34**, 1090 (1964).

(23) The qualitatively observed difference of rates of hydrolysis of the lactones **17** was in agreement with their designated stereochemistry. The near-absence of steric interference and encouragement by the carbon–chlorine dipole makes hydration of the carbonyl group of lactone **17b** preferred over such reaction of **17a**. Hydrolysis of the former took place much more rapidly than saponification of the latter lactone.

(24) K. Auwers and F. von der Heyden, *Ber.*, **42**, 2404 (1909).

(25) C. E. Berkoff and L. Crombie, *J. Chem. Soc.*, 3734 (1960).



27a 27b

Experimental Section

Melting points were determined on a Reichert micro-hot stage and are uncorrected. Infrared spectra were obtained on Perkin-Elmer Model 137 and 137B spectrophotometers. Ultraviolet spectra were recorded on a Cary Model 14 spectrophotometer. Proton magnetic resonance spectra of deuteriochloroform solutions (unless otherwise noted) containing tetramethylsilane (δ = 0 ppm) as internal standard were taken on Varian Associates Model A-60 and HA-100 spectrometers. Solvent shift studies were carried out on 3% solutions.

3-Isopropyl-6-methyl-6-dichloromethyl-2,4-cyclohexadienone (1b). A solution of 13.2 g of sodium hydroxide in 25 ml of water was added dropwise over a 0.5-hr period to a stirring solution of 10.0 g of carvacrol [δ (pmr) 1.12 (d, 6, J = 7.0 cps, *i*-Pr methyls), 2.18 (s, 3, C-Me), 2.72 (septet, 1, J = 7.0 cps, *i*-Pr methine), 6.58 (d, 1, J = 2.0 cps, H-6), 6.65 (q, 1, J = 2.0, 7.5 cps, H-4), 6.98 (d, 1, J = 7.5 cps, H-3)] in 24 ml of chloroform and the mixture stirred and mildly refluxed for 2.5 hr. Water, 100 ml, was added to the cooled mixture, the organic phase separated, and the aqueous solution extracted with chloroform. The combined chloroform solutions were washed with water and with saturated brine solution and dried over sodium sulfate. The solution was evaporated under vacuum and the black residual gum dissolved in 200 ml of petroleum ether. The solution was extracted exhaustively with Claisen alkali, washed with water and brine, dried, and evaporated under vacuum. Chromatography of the light brown oily residue, 2.4 g, on neutral alumina (activity 1) and elution with 1:1 benzene–petroleum ether gave 2.2 g of pale yellow oil whose distillation (80–90° (0.35 Torr)) led to 1.2 g of ketone **1b**: infrared (neat) C=O 6.01 (s), C=C 6.10 μ (s); ultraviolet (95% EtOH) λ_{max} 303 mμ (ϵ 5080); pmr δ 1.15 (d, 6, J = 7.0 cps, *i*-Pr methyls), 1.30 (s, 3, Me), 2.57 (septet, 1, J = 7.0 cps, *i*-Pr methine), 5.90 (d, 1, J = 2.0 cps, H-2), 6.05 (s, 1, $CHCl_2$), 6.40 (q, 1, J = 2.0, 10.0 cps, H-4), 6.63 (d, 1, J = 10.0 cps, H-5). The substance was used immediately for reactions without further purification.

2-Methyl-2-dichloromethyl-5-isopropyl-3-cyclohexenone (5b). Repetition of the Auwers synthesis[24] (without the use of methyl iodide as initiator of the Grignard reaction) led to a 86% yield of a 3:2 epimer mixture of ketones **5b**: bp 82–86° (5 Torr); infrared (neat) C=O 5.82 (s), C=C 6.01 μ (w); pmr δ 0.95 (d, 6, J = 7.0 cps, *i*-Pr methyls), 1.31 (s, 3, Me), 6.02 (s, 1, $CHCl_2$ of minor component), 6.12 (s, 1, $CHCl_2$ of major component), 5.85 (m, 1, J = 10.0 cps, H-4), 6.11 (m, 1, J = 10.0 cps, H-3).

Anal. Calcd for $C_{11}H_{16}OCl_2$: C, 56.15; H, 6.86. Found: C, 56.18; H, 6.91.

3-Isopropyl-6-methyl-6-dichloromethyl-2-cyclohexenone (3b). Repetition of the Auwers procedure[24] afforded a 75% yield of ketone **3b**: bp 102–105° (0.5 Torr); infrared (neat) C=O 6.03 (s), C=C 6.17 μ (s); pmr δ 1.13 (d, 6, J = 7.0 cps, *i*-Pr methyls), 1.25 (s, 3, Me), 5.85 (d, 1, J = 1.5 cps, olefinic H), 6.31 (s, 1, $CHCl_2$).

Anal. Calcd for $C_{11}H_{16}OCl_2$: C, 56.15; H, 6.86. Found: C, 56.20; H, 6.80.

Hydrogenations of Unsaturated Ketones. A mixture of 5.00 g of ketone **1a** and 0.5 g of 10% palladium–charcoal in 15 ml of 95% ethanol was hydrogenated at room temperature and atmospheric pressure. After the uptake of 1.2 moles of hydrogen the mixture was filtered and the filtrate evaporated. Chromatography of the residue, 4.80 g (*ca.* 15% of **4** by pmr analysis[26]), on Florisil and elution with 9:1 petroleum ether–benzene gave 790 mg of a mixture containing 50% **4**, while further elution yielded 3.8 g of a mixture containing preponderantly **3a**. Rechromatography of 500 mg of the mixture enriched in **4** on Florisil, elution with 50:1 petroleum ether–benzene, and distillation (bath temperature 45° (0.2 Torr)) of the eluate, 70 mg, yielded 6-methyl-6-dichloromethyl-3-cyclohexenone (**4**): infrared (neat) C=O 5.81 (s), C=C 5.97 μ (w); pmr δ 1.36 (s, 3, Me), 5.83 (m, 2, olefinic Hs), 6.30 (s, 1, $CHCl_2$).

Anal. Calcd for $C_8H_{10}OCl_2$: C, 49.76; H, 5.23. Found: C, 49.46; H, 5.34.

Ketone **4**, 30 mg, was added to 200 mg of ice-cold concentrated sulfuric acid and the mixture stirred at room temperature for 10 hr. Ice was added and the mixture extracted with ether. The extract was washed with sodium bicarbonate solution and water, dried, and evaporated. This yielded 28 mg of liquid 6-methyl-6-dichloromethyl-2-cyclohexenone (**3a**): bp 63° (0.35 Torr); infrared (neat) C=O 5.98 (s), C=C 6.05 (m), 6.16 μ (w); pmr δ 1.29 (s, 3, Me), 6.00 (d of t, J = 10.0, 2.0 cps, H-2), 6.32 (s, 1, $CHCl_2$), 7.00 (d of m, 1, J = 10.0 cps, H-3).

Anal. Calcd for $C_8H_{10}OCl_2$: C, 49.76; H, 5.23. Found: C, 49.77; H, 5.44.

The identical reaction with 3.80 g of ketone **5a** and 17 ml of concentrated sulfuric acid yielded 3.27 g of ketone **3a**.

A mixture of 39.0 g of ketone **3b** and 3.0 g of 10% palladium–charcoal in 200 ml of ethanol was hydrogenated at room temperature and atmospheric pressure. The mixture was filtered and the filtrate evaporated under vacuum. Refrigeration of the oily residue (9:1 of **2b** and **2c**, respectively, by pmr analysis) for 18 hr and subsequent trituration with cold petroleum ether gave 32.8 g of a crystalline solid whose crystallization from methanol yielded colorless leaflets of ketone **2b**: mp 65–66°; infrared (CCl_4) C=O 5.82 μ (s); pmr δ 0.92 (d, 6, J = 6.5 cps, *i*-Pr methyls), 1.27 (s, 3, Me), 6.31 (s, 1, $CHCl_2$).

Anal. Calcd for $C_{11}H_{18}OCl_2$: C, 55.69; H, 7.65. Found: C, 55.38; H, 7.75.

A mixture of 422 mg of ketone **1b** and 48 mg of 10% palladium–charcoal in 35 ml of ethanol was hydrogenated at room temperature and atmospheric pressure. The mixture was filtered and the filtrate evaporated under vacuum. Pmr analysis of the residue showed it consisted of a 4:1 mixture of ketones **2b** and **2c**, respectively. Crystallization as above yielded crystalline ketone **2b**, mp 65–66°.

2-Methyl-2-dichloromethyl-3-cyclohexenone (5a). Sodium borohydride, 30 g, was added in portions to an ice-cold solution of 72 g of ketone **1a** in 750 ml of absolute ethanol. The mixture was stirred at room temperature for 12 hr, whereupon the excess hydride was decomposed by the cautious addition of 10% hydrochloric acid. Water, 1 l., was added and the mixture extracted with ether. The extract was washed successively with water, 10% potassium hydroxide solution, and water, dried, and evaporated. Crystallization of the residue, 70 g, from hexane gave an alcohol: mp 61–62°; infrared (Nujol) OH 2.99 (m), C=C 6.08 μ (w); pmr δ 1.21 (s, 3, Me), 4.04 (m, 1, oxymethine), 5.78 (m, 2, olefinic Hs), 6.05 (s, 1, $CHCl_2$).

Anal. Calcd for $C_6H_{12}OCl_2$: C, 49.25; H, 6.20. Found: C, 49.01; H, 6.32.

Jones reagent,[27] 0.8 ml, was added to a cold, stirring solution of 1.2 g of the alcohol in 12 ml of acetone at such a rate as to keep the temperature at −5 to −3°. The mixture was stirred for 0.5 hr, 25 ml of water added, and the mixture extracted with ether. The extract was washed successively with water, 10% potassium hydroxide solution, and water, dried, and evaporated. Crystallization of the residue from hexane gave 0.95 g of ketone **5a**: mp 77–78°; infrared (Nujol) C=O 5.88 μ (s); pmr δ 1.31 (s, 3, Me), 2.4–2.6 (n, 4, α-keto and allyl methylenes), 5.7–6.3 (m 2, olefinic Hs), 6.12 (s, 1, $CHCl_2$).

Anal. Calcd for $C_8H_{10}OCl_2$: C, 49.77; H, 5.23. Found: C, 49.85; H, 5.33.

2-Methyl-2-chloromethylcyclohexanone (6). A solution of 10.00 g of ketone **2a** [pmr δ 1.30 (s, 3, Me), 6.29 (s, 1, $CHCl_2$)] and 17.0 g of tri-*n*-butyltin hydride was heated in a sealed ampoule at 165° for 40 hr. Filtration of the mixture and distillation (83–85° (4.3 Torr)) yielded 6.36 g of crude **6**. Chromatography of the distillation residue on silica gel and elution with 9:1 petroleum ether–ether gave 1.53 g of impure **6**. Rechromatography of the combined products on silica gel and elution with benzene led to 6.57 g of pure, liquid ketone **6**: infrared (neat) C=O 5.84 μ (s); pmr δ 1.20 (s, 3, Me), 3.66 (s, 2, CH_2Cl). The semicarbazone was crystallized from methanol and showed mp 156.5–157° (lit.[6] mp 146–147° dec); the melting point was undepressed on admixture of the derivative with an authentic sample.[28]

(26) The yield of **4** was variable (10–40%).

(27) A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *J. Chem. Soc.*, 2555 (1953).

(28) The authors are indebted to Professor C. R. Johnson for a gift of this substance.

1-Methylbicyclo[3.1.1]heptan-6-one (7a). A solution of 2.50 g of ketone **6** in 5 ml of dry *t*-butyl alcohol was added dropwise over a 2-hr period to a potassium *t*-butoxide solution (750 mg of potassium in 30 ml of dry *t*-butyl alcohol) under nitrogen at 65°. After being stirred at 65° for an additional 2 hr the mixture was poured into 50 ml of water and extracted with petroleum ether. Acidification of the aqueous solution and usual work-up yielded 370 mg of nonolefinic (by pmr analysis) acidic material which was not investigated further. The organic extract was washed with 5% potassium hydroxide solution and with water, dried, and evaporated by solvent removal at atmospheric pressure through distillation in an 8-in. vacuum-jacketed column. Distillation (47° (5.5 Torr)) of the residue gave 832 mg of a mixture shown by gpc analysis (5 ft × 1/8 in. Carbowax column at 90°) to consist of 95% **7a**[7] (retention time 10.4 min) and 4% 1-methylbicyclo[3.2.0]heptan-6-one (**8**)[7] (retention time 8.8 min).

A mixture of 800 mg of ketone **7b** (*vide infra*), 1.60 g of freshly distilled tri-*n*-butyltin hydride, and 60 mg of α,α'-azobisisobutyronitrile was heated in a sealed ampoule at 90° under nitrogen for 5 hr. Distillation (46° (3.5 Torr)) of the mixture gave 330 mg of 1-methylbicyclo[3.1.1]heptan-6-one (**7a**):[7] infrared (neat) C=O 5.63 μ (s); pmr δ 1.09 (s, 3, Me), 3.00 (m, 1, α-ketomethine).

1-Methyl-7-chlorobicyclo[3.1.1.]heptan-6-one (7b). A solution of 15.00 g of ketone **2a** in 30 ml of dry *t*-butyl alcohol was added dropwise over a 2-hr period to a potassium *t*-butoxide solution (3.60 g of potassium in 120 ml of *t*-butyl alcohol) under nitrogen at 65°. Some alcohol, 120 ml, was removed by distillation at atmospheric pressure through an 8-in. vacuum-jacketed column and 100 ml of 5% sodium bicarbonate solution added. The mixture was extracted exhaustively with petroleum ether and the extract washed with water and dried. The aqueous solution was brought to pH 8 by the addition of 10% hydrochloric acid, concentrated by removal of 80 ml of water by distillation, acidified to pH 5, and extracted with ether. The latter extract led to 630 mg of an acid mixture shown by pmr analysis to consist predominantly of acid **9b** and contaminated by small amounts of the acid analogs of **10**. Gpc analysis of the petroleum ether extract of neutral products (5 ft × 1/8 in. 5% SE30 column at 110 and 148°, fluorene was used as internal standard, differences in molar response to the detector were corrected) revealed the presence of five components: 73% **7b** (110°, retention time 4.3 min), 11% **9a** (20.5 min), 4% starting ketone **2a** (9.6 min), 3% **10b** (5.2 min), and 1.4% **10a** (6.2 min).

Removal of the solvent of the petroleum ether extract by atmospheric distillation through an 8-in. vacuum-jacketed column and distillation (45–75° (0.2 Torr)) of the residue led to 9.51 g of distillate and 2.03 g of residual oil. Distillation of the latter gave 1.32 g of acyclic ester whose purification by redistillation (115° (3.5 Torr)) yielded liquid *t*-butyl 6-methyl-7-chloro-6-heptenoate (**9a, 12a**): infrared (neat) C=O 5.78 (s), C=C 6.10 μ (w); pmr δ 1.44 (s, 9, *t*-Bu).

Anal. Calcd for $C_{12}H_{21}O_2Cl$: C, 61.93; H, 9.09. Found: C, 61.72; H, 8.95.

Chromatography of the low-boiling distillate on Florisil and elution with petroleum ether gave 168 mg of bicyclic ester whose purification by rechromatography on Florisil and distillation (bath temperature 60° (3.5 Torr)) yielded liquid *t*-butyl *exo*-bicyclo[3.1.0]-hexane-6-carboxylate (**10b**): infrared (neat) C=O 5.82 μ (s); infrared ($CDCl_3$) cyclopropane CH 1.693 μ (w); pmr δ 1.30 (s, 3, Me), 1.43 (s, 9, *t*-Bu).

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.64; H, 10.12.

Continued elution with petroleum ether gave 338 mg of bicyclic ester whose purification (as that of **10b**) yielded liquid *t*-butyl *endo*-bicyclo[3.1.0]hexane-6-carboxylate (**10a**): infrared (neat) C=O 5.80 μ (s); infrared ($CDCl_3$) cyclopropane CH 1.693 μ (w); pmr δ 1.24 (s, 3, Me), 1.43 (s, 9, *t*-Bu).

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.25; H, 10.24.

Continued elution with 9:1 petroleum ether–ether gave a ketone whose distillation (85° (4.3 Torr)) yielded 6.42 g of pure 1-methyl-7-chlorobicyclo[3.1.1]heptan-6-one (**7b**):[8] infrared (neat) C=O 5.60 μ (s); pmr δ 1.15 (s, 3, Me).

A solution of 600 mg of ester **9a** (**12a**) and 500 mg of potassium hydroxide in 15 ml of water and 15 ml of dioxane was kept at 80° for 18 hr. Water, 100 ml, was added and the mixture washed exhaustively with ether. The aqueous solution was acidified with 10% hydrochloric acid and extracted with ether. The extract was dried and evaporated. Conversion of the resultant acid **9b**, 480 mg, into an amide by standard procedure yielded crystals, mp 63.5–64° (from hexane) (lit.[9] mp 65.5–66.5°).

1-Methyl-4-isopropylbicyclo[3.1.1]heptan-6-ones (7c and 7d). A solution of 2.25 g of ketone **2b** and potassium *t*-butoxide (from 0.76 g of potassium) in 20 ml of dry *t*-butyl alcohol was kept at room temperature for 45 hr. Water was added and the mixture extracted exhaustively with ether. Acidification of the aqueous solution led to 0.3 g of acidic products which were not investigated further. The ether extract was washed with water, dried, and evaporated. Semicarbazone formation of the residue, 1.46 g, and crystallization of the derivative, 1.18 g, from ethanol gave colorless plates of **semicarbazone of 7c**, mp 218–220°.

Anal. Calcd for $C_{12}H_{20}ON_3Cl$: N, 16.30. Found: C, 16.18.

Regeneration of ketone from 1.13 g of the semicarbazone by the use of levulinic acid[29] and distillation of the product yielded 0.78 g of **7c**: bp 70–71° (3 Torr); infrared (neat) C=O 5.60 μ (s); pmr δ 0.94 (d, 6, J = 7.0 cps, *i*-Pr methyls), 1.12 (s, 3, Me), 3.09 (d, 1, J = 2.0 cps, α-ketomethine), 4.41 (s, 1 CHCl).

Anal. Calcd for $C_{11}H_{17}OCl$: C, 65.82; H, 8.54. Found: C, 66.01; H, 8.81.

A solution of 2.11 g of ketone **1b** and 4.5 g of sodium carbonate in 50 ml of dry dimethyl sulfoxide was kept at 85° under nitrogen for 24 hr. The cooled solution was diluted with 150 ml of water and extracted exhaustively with petroleum ether. The extract was washed with 10% sodium carbonate solution, cold water, and saturated brine solution, dried, and evaporated. Rapid passage of a benzene solution of the residual oil, 1.62 g, through an alumina (activity II) column gave a material suitable for the next reaction. Purification of the product was executed by distillation, chromatography on Florisil and elution with 3:1 petroleum ether–benzene, and distillation (bath temperature 110° (0.15 Torr)) of the center eluates. This led to liquid **21**: infrared (neat) C=O 5.59 μ (s); pmr δ 1.30 (s, 3, saturated Me), 1.78 (d, 3, J = 1.0 cps, olefinic Me), 1.79 (s, 3, olefinic Me), 4.19 (s, 1, CHCl), 4.22 (d, 1, J = 2.0 cps, α-ketomethine), 5.87 (broad d, 1, J = 8.5 cps), 6.52 (q, 1, J = 8.5, 2.0 cps) (olefinic Hs).

Anal. Calcd for $C_{11}H_{13}OCl$: C, 67.17; H, 6.66. Found: C, 66.94; H, 6.74.

A mixture of 1.62 g of **21** and 0.32 g of 10% palladium–charcoal in 30 ml of 95% ethanol was hydrogenated at room temperature and atmospheric pressure. Upon cessation of hydrogen uptake the mixture was filtered and the filtrate evaporated. Chromatography of the residue, 1.48 g, on silica gel and elution with 3:1 petroleum ether–benzene gave 1.10 g of colorless oil whose distillation (bath temperature 80° (0.15 Torr)) yielded liquid **7d**: infrared (neat) C=O 5.59 μ (s); pmr δ 0.89 (d, 6, J = 7.0 cps, *i*-Pr methyls), 1.13 (s, 3, Me), 3.09 (d, 1, J = 2.0 cps, α-ketomethine), 3.94 (s, 1, CHCl).

Anal. Calcd for $C_{11}H_{17}OCl$: C, 65.82; H, 8.54. Found: C, 65.95; H, 8.76.

Semicarbazone formation of the ketone and crystallization of the derivative from benzene gave colorless needles of **semicarbazone of 7d**, mp 193–194°.

Anal. Calcd for $C_{12}H_{20}ON_3Cl$: C, 55.90; H, 7.82; N, 16.30. Found: C, 56.16; H, 7.93; N, 16.46.

A mixture of 8.90 g of ketone **5b** stereoisomers and 0.50 g of 10% palladium–charcoal in 90 ml of 95% ethanol was hydrogenated at room temperature and atmospheric pressure. Upon cessation of hydrogen uptake the mixture was filtered and the filtrate evaporated. Chromatography of the oily residue, 8.90 g, whose pmr analysis revealed it to be 3:2 **2c–2b**, on alumina and elution with 20:1 hexane–ether yielded first 3.2 g of solid **2b**, 0.8 g of a semisolid mixture, and 4.60 g of an oil whose pmr spectrum showed it to be a mixture of **2b** and **2c** highly enriched in the latter. A solution of the last fraction and potassium *t*-butoxide (from 1.51 g of potassium) in 45 ml of dry *t*-butyl alcohol was kept at room temperature for 72 hr. Water was added and the mixture extracted with ether. The extract was washed with water, dried, and evaporated. The residual, oily ketone, 3.50 g, was derivatized by standard procedure. Crystallization of the semicarbazone, 1.34 g, from benzene gave **semicarbazone of 7d**, mp 193–194°. Liberation of ketonic material by the levulinic acid procedure[29] yielded 0.92 g of ketone **7d**.

Lactones 17. An ice-cold mixture of 1.85 g of ketone **7b**, 5 ml of trifluoroacetic anhydride, 1 ml of 85% hydrogen peroxide, and 2.0 g of disodium hydrogen phosphate in 5 ml of dry methylene chloride was kept at room temperature for 20 hr. The mixture was washed with a saturated solution of sodium bicarbonate, the washings were extracted with methylene chloride, and the combined

(29) C. H. DePuy and B. W. Ponder, *J. Am. Chem. Soc.*, **81**, 4629 (1959).

organic solutions were evaporated. Crystallization of the solid residue, 1.98 g, mp 130–132°, from carbon tetrachloride and sublimation yielded lactone **17a**: mp 132–133°; infrared (Nujol) C=O 5.62 μ (s); pmr δ 1.53 (s, 3, Me), 2.95 (m, 1, α-ketomethine), 4.17 (s, 1, CHCl).

Anal. Calcd for $C_8H_{11}O_2Cl$: C, 54.86; H, 6.29. Found: C, 54.95; H, 6.33.

A solution of 3.72 g of lactone **17a** in 200 ml of methanol and 50 ml of 50% aqueous potassium hydroxide was kept under nitrogen at room temperature for 24 hr. After addition of 29 ml of concentrated hydrochloric acid and 20 ml of water the mixture was concentrated and extracted with methylene chloride. The aqueous solution was acidified with 10% hydrochloric acid to pH 3 and extracted with ether. The extract was washed with saturated brine solution, dried, and evaporated. Crystallization of the solid residue, 3.21 g, from ethyl acetate gave 3-hydroxy-3-methyl-1-cyclohexenecarboxylic acid (**19**): mp 138–139°; infrared (Nujol) OH 2.92 (m), 3.08 (m), 3.82 (w), C=O 5.89 (s), 5.95 (m), C=C 6.07 μ (m); pmr (deuterioacetone) δ 1.30 (s, 3, Me), 6.72 (t, 1, J = 2.0 cps, olefinic Hs).

Anal. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.75. Found: C, 61.69; H, 7.73.

A mixture of 250 mg of lactone **17a** and 95 mg of sodium hydroxide in 10 ml of water and 20 ml of ether was stirred at room temperature for 24 hr. Drying and distillation of the ether layer led to the recovery of 122 mg of starting lactone. Acidification of the aqueous layer with 10% hydrochloric acid to pH 4, extraction with 1:1 methylene chloride–ether, and evaporation of the extract gave 110 mg of acid **18a**: infrared (Nujol) OH 2.90 (s), 3.1–3.3 (m), C=O 5.82 μ (s); pmr (sodium hydroxide solution of D_2O, methanol as internal standard) δ 120 cps upfield (s, 3, Me), 30 cps upfield (m, 1, carboxymethine), 64 cps downfield (d, 1, J = 3.0 cps, CHCl). A solution of 50 mg of **18a** and 1 ml of 50% potassium hydroxide in 2 ml of methanol was kept at room temperature for 24 hr. Upon addition of 5 ml of water the mixture was extracted with methylene chloride. The aqueous solution was acidified with 10% hydrochloric acid and extracted with 1:1 ether–methylene chloride. Drying of the extract and evaporation yielded 35 mg of crystalline **19**.

Lithium wire was added to a mixture of 2.25 g of acid **19** in 30 ml of tetrahydrofuran and 100 ml of liquid ammonia until a blue color persisted. Ammonium chloride was added 10 min thereafter and the ammonia was allowed to evaporate. Ice–water was added and the solution acidified with 10% hydrochloric acid to pH 3 and extracted with ether. Drying and evaporation of the extract led to 1.77 g of liquid 3-methyl-2-cyclohexenecarboxylic acid (**20**): infrared (neat) OH 3.0–3.3 (m), C=O 5.84 μ (s); pmr δ 1.69 (broad s, 3, Me), 5.52 (m, 1, olefinic H). Its derivative was prepared by standard procedure. Crystallization from ether gave *p*-bromophenacyl 3-methyl-2-cyclohexenecarboxylate: mp 79–80°; infrared (Nujol) C=O 5.72 (s), 5.88 (s), C=C 6.27 (m), 6.33 μ (w); pmr δ 1.69 (broad s, 3, Me), 3.21 (m, 1, α-ketomethine), 5.26 (s, 2, α-ketomethylene), 5.52 (m, 1, olefinic H).

Anal. Calcd for $C_{16}H_{17}O_3Br$: C, 56.99; H, 5.05. Found: C, 56.89; H, 5.11.

Reagent grade (Allied Chemical Co.) sodium hypochlorite solution, 3.0 ml, was added over a 5-min period to an ice-cold mixture of 70 mg of acid **20** and 500 mg of sodium dihydrogenphosphate hexahydrate in 20 ml of methylene chloride. The mixture was diluted with water, basified with 10% sodium hydroxide solution, and extracted with ether. The extract was washed with 10% sodium hydroxide and with water, dried, and evaporated. Gpc analysis (5 ft × 1/8 in. 5% SE30 column at 155°) of the residue, 60 mg, showed it to be a mixture containing a lactone of retention time 1.6 min (contrastingly, the retention time of **17a** was 2.6 min). Preparative gpc (10 ft × 3/8 in. 30% SF96 column at 185°, helium flow at 270 ml/min) yielded 37 mg of lactone **17b**: mp 32°, retention time 21 min; infrared (neat) C=O 5.58 μ (s); pmr δ 1.42 (s, 3, Me), 2.75 (m, 1, α-ketomethine), 4.29 (broad d, 1, J = 5.0 cps, CHCl).

A solution of 500 mg of lactone **17b** and 3.50 g of potassium hydroxide in 30 ml of methanol and 3.5 ml of water was kept at room temperature for 24 hr. Work-up as in the conversion of **17a** into **19** and crystallization of the product from ethyl acetate gave 352 mg of acid **19**, mp 137–139°. A mixture of 200 mg of lactone **17b** and 200 mg of sodium hydroxide in 25 ml of ether and 5 ml of water was stirred at room temperature for 40 min. Drying and evaporation of the ether layer led to the recovery of 24 mg of starting lactone. Work-up of the aqueous solution as in the conversion of **17a** into **18a** and crystallization of the product, 154 mg, from benzene–ethyl acetate gave acid **18b**: mp 164–165° dec; infrared (Nujol) OH 2.98 (s), C=O 5.88 μ (s); pmr (sodium hydroxide solution of D_2O, methanol as internal standard) δ 121 cps upfield (s, 3, Me), 25–48 cps upfield (m, 1, carboxymethine), 4 cps downfield (d, 1, J = 3.0 cps, CHCl). Base treatment of 50 mg of **18b** according to the procedure of the conversion of **18a** into **19** yielded 36 mg of acid **19**.

Lactones 23 and 25. A mixture of 500 mg of lactone **22a**,[25] sodium hydride (from 700 mg of a 53% dispersion), and 3 ml of ethyl formate in 10 ml of dry benzene was stirred at room temperature for 18 hr. Methanol was added for the destruction of excess hydride and the solution poured into water. The aqueous solution was acidified with 10% hydrochloric acid and extracted with ether. Evaporation of the extract and trituration of the residue, 570 mg, gave 420 mg of crystals, mp 125–128°, whose recrystallization from methanol yielded colorless prisms of **22b**: mp 127–128°; infrared spectrum (Nujol) C=O 5.95 (s), C=C 6.15 μ (s); intensely purple in ferric chloride solution.

Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.91; H, 8.99. Found: C, 70.08; H, 8.74.

An excess of ozone was passed through an ice-cold solution of 1.04 g of lactone **22b** in 10 ml of acetic acid and 10 ml of ethyl acetate. Thereupon 3 ml of 30% hydrogen peroxide solution was added and the mixture kept at room temperature for 18 hr. Water was added and the mixture extracted with ether. The extract was washed with sodium carbonate solution and with water, dried, and evaporated. Chromatography of the residue, 0.68 g, on alumina and elution with 4:1 hexane–ether yielded 141 mg of oil whose distillation (bath temperature 110° (0.5 Torr)) led to liquid lactone **23**: infrared spectrum (neat) C=O 5.65 μ (s).

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96. Found: C, 72.16; H, 9.88.

A solution of 1.4 ml of trifluoroacetic anhydride and 0.2 ml of 90% hydrogen peroxide in 2 ml of methylene chloride was added to a suspension of 3.3 g of disodium hydrogen phosphate and 274 mg of ketone **7d** in 4 ml of methylene chloride and the mixture stirred at 50° for 19 hr. It was filtered and the filtrate washed with 10% sodium carbonate solution and with water and evaporated. Chromatography of the residue on alumina and elution with 20:1 hexane–ether yielded 85 mg of starting ketone. Elution with 9:1 to 1:1 hexane–ether led to 59 mg of a crystalline solid whose recrystallization from hexane gave colorless needles of lactone **25a**: mp 94–95°; infrared (Nujol) C=O 5.63 μ (s); pmr δ 0.89 (d, 3, J = 7.0 cps, Me of *i*-Pr), 1.02 (d, 3, J = 7.0 cps, Me of *i*-Pr), 1.52 (s, 3, Me), 3.07 (broad s, 1, α-ketomethine), 4.02 (s, 1, CHCl).

Anal. Calcd for $C_{11}H_{17}O_2Cl$: C, 60.95; H, 7.91. Found: C, 61.00; H, 7.93.

A solution of 129 mg of ketone **7c**, 648 mg of *m*-chloroperbenzoic acid, and 1 drop of concentrated sulfuric acid in 1 ml each of acetic acid and methylene chloride was kept at room temperature for 96 hr. Water was added and the mixture extracted with ether. The extract was washed with 2% sodium hydroxide solution and with water and evaporated. Crystallization of the residue, 132 mg, from hexane gave colorless leaflets of lactone **25b**: mp 43.5–45°; infrared (Nujol) C=O 5.61 μ (s); pmr δ 0.9–1.1 (m, 6, *i*-Pr methyls), 1.52 (s, 3, Me), 3.00 (m, 1, α-ketomethine), 4.25 (s, 1, CHCl).

Anal. Calcd for $C_{11}H_{17}O_2Cl$: C, 60.95; H, 7.91. Found: C, 61.03; H, 7.97.

Glycols 24. A mixture of 153 mg of lactone **23** and 100 mg of lithium aluminum hydride in 2 ml of anhydrous ether was refluxed for 1 hr. Water and 10% hydrochloric acid solution were added successively and the mixture was extracted with ether. The extract was dried and evaporated. Crystallization of the crystalline residue, 153 mg, mp 64–67°, from hexane gave colorless plates of diol **24a**: mp 66.5–67.5°; infrared spectrum (Nujol) OH 3.15 μ (s).

Anal. Calcd for $C_{11}H_{22}O_2$: C, 70.92; H, 11.90. Found: C, 70.55; H, 11.56.

A mixture of 35 mg of lactone **25a** and 100 mg of lithium aluminum hydride in 2 ml of dry tetrahydrofuran was refluxed for 18 hr. Work-up as above yielded 35 mg of crude product whose purification by preparative tlc on a thick plate of silica gel led to 8 mg of crystals, mp 63–65°. Crystallization from hexane yielded a product whose melting point (no depression of mixture melting point) and infrared spectrum were those of diol **24a**.

A mixture of 106 mg of lactone **25b** and 100 mg of lithium aluminum hydride in 3 ml of dry tetrahydrofuran was refluxed for 18 hr. Work-up as above and crystallization of the crude product from hexane–benzene yielded 35 mg of crystalline alcohol. Recrystallization led to colorless plates of diol **24b**: mp 109–110°; infrared (Nujol) OH 3.04 μ (s); pmr δ 0.79 (d, 3, J = 7.0 cps, Me of *i*-Pr),

0.92 (d, 3, J = 7.0 cps, Me of i-Pr), 1.22 (s, 3, Me), 3.60 (m, 2, oxymethylene).

Anal. Calcd for $C_{11}H_{22}O_2$: C, 70.92; H, 11.90. Found: C, 70.63; H, 11.92.

Acknowledgment. The authors are indebted to Eli Lilly and Co. and the National Science Foundation for support of this investigation.

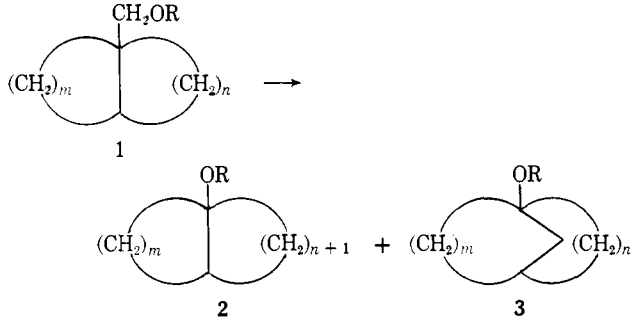
Solvolysis of Bicyclo[4.2.0]octane-1-methyl *p*-Toluenesulfonate[1a]

William G. Dauben and James L. Chitwood[1b]

Contribution from the Department of Chemistry, University of California, Berkeley, California 94720. *Received April 10, 1969*

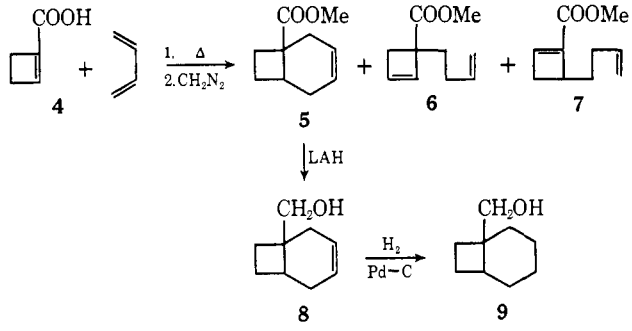
Abstract: Bicyclo[4.2.0]octane-1-methanol (**9**) was synthesized in a three-step reaction sequence from the Diels–Alder adduct of 1-cyclobutene-1-carboxylic acid (**4**) and butadiene *via* methyl bicyclo[4.2.0]oct-3-ene-1-carboxylate (**5**) and bicyclo[4.2.0]oct-3-ene-1-methanol (**8**). The *p*-toluenesulfonate ester **10** underwent solvolysis in buffered acetic acid to yield 90% of 1-bicyclo[4.2.1]nonyl acetate (**12c**) and 10% of 1-bicyclo[4.2.1]nonyl *p*-toluenesulfonate (**12d**). The rate of the reaction was determined at 41.6 and 60.6° and the calculated rate at 100° is 1.0×10^4 faster than the rate of neopentyl *p*-toluenesulfonate. The effects of conformation, ring size, and strain on the course and rate of these neopentyl-type rearrangements are discussed.

Recently a correlation between hydrocarbon strain release and solvolysis rate was reported for a series of bicyclo[$m.n.0$]alkane-1-methanols (**1**) as being indicative of alkyl participation in neopentyl rearrangements.[2] As m and n get smaller, the rearrangement rate increases and the type of product changes from **2** to **3**. The effects of conformation, ring size, and strain on the course, as well as the rate, of these neopentyl-type rearrangements continues to be of interest.



Bicyclo[4.2.0]octane-1-methanol (**9**), an interesting system in its own right, is of particular interest here since it provides an additional check for the strain release–rate correlation and since it is a neopentyl system in which the maximum hydrocarbon strain release should give expansion of the smaller ring leading to **2** (m = 4, n = 3) rather than expansion of both rings simultaneously (bridging) leading to **3** (m = 4, n = 2).

Syntheses. 1-Cyclobutene-1-carboxylic acid (**4**) was allowed to react with butadiene under pressure at 120° and the resulting acidic products were esterified. Methyl bicyclo[4.2.0]oct-3-ene-1-carboxylate (**5**) was obtained by spinning-band distillation or vpc. Two minor components (4% acidic fraction) were most likely "ene" reaction products[3] of butadiene and **4** since



(1) they were isomeric with the major product, (2) their spectra match the suggested structural assignments; in particular, they had two sets of olefinic protons in the nmr whose patterns were consistent with the assignment, and (3) hydroboration and Jones oxidation of the mixture of alcohols indicated that the cyclobutane ring was still intact and that it contained one of the double bonds, since cyclobutanone derivatives were obtained ($\nu_{C=O}^{CCl_4}$ 1780 cm^{-1}). These two minor components were formed in approximately equal amounts. The minor component whose vpc retention time was less than that of **5** was assigned structure **6**; the minor component of longer retention time (almost twice as long as **5**) was assigned structure **7**. The infrared spectrum of the conjugated ester **7** showed a 1705-cm^{-1} ester band, and its nmr spectrum showed only one cyclobutenyl hydrogen. The unconjugated ester **6**, however, had a vpc retention time similar to that of **5**, its infrared spectrum showed a normal, unconjugated ester band at 1735 cm^{-1}, and its nmr spectrum showed two cyclobutenyl hydrogens.

The ester **5** was reduced with lithium aluminum hydride to bicyclo[4.2.0]oct-3-ene-1-methanol (**8**) and **8** was catalytically hydrogenated to bicyclo[4.2.0]-octane-1-methanol (**9**). The *p*-toluenesulfonate ester of **9** was prepared from *p*-toluenesulfonyl chloride in pyridine and **9**.

(1) (a) This work was supported in part by Grant GP-3890 from the National Science Foundation; (b) National Institutes of Health Predoctoral Fellow, 1966–1968.

(2) W. G. Dauben, J. L. Chitwood, and K. V. Scherer, Jr., *J. Amer. Chem. Soc.*, **90**, 1014 (1968).

(3) For a recent review see: J. A. Berson, R. G. Wall, and H. D. Perlmutter, *ibid.*, **88**, 187 (1966); and the references therein.