Experimental Section

Melting points are uncorrected. High-purity commercial solvents were employed for all spectral determinations. Infrared and ultraviolet spectra were recorded with a Perkin-Elmer Model 337 and a Cary Model 14 recording spectrophotometer, respectively. Mass spectra were obtained on a Hitachi RMU-6D mass spectrometer. The nmr spectra were recorded on a Bruker HFX-10 (90 MHz) or a Varian A-60A (60 MHz) instrument with variable-temperature capability. Line shapes were calculated by a CDC-6600 computer using the DNMR program developed by Binsch.[14] The rate-dependent *tert*-butyl resonances of **6** were simulated for the azide moiety exchanging among three equivalent sites. High-quality experimental spectra were obtained on the Bruker HFX-10 instrument by constantly checking the field homogeneity with an internal standard. The same scale (2.00 Hz/cm) was employed for both the experimental and computer-simulated spectra. Sample temperatures were determined by the chemical shift method employing a capillary containing methanol (or ethylene glycol) which was inserted into the sample tube. Reference to revised calibration curves provided the temperatures.[14c,24]

1,2,3-Tri-*tert*-butyl-3-azidocyclopropene (6).—To a solution of 1.00 g (3.28 mmol) of tri-*tert*-butylcyclopropenyl perchlorate in 10 ml of acetonitrile was added 0.228 g (3.51 mmol) of sodium azide (Matheson Coleman and Bell) in one portion. The mixture was stirred at 0° for 1 hr, after which dilution with 50 ml of water resulted in the separation of a colorless oil. The oil was then extracted into two 15-ml portions of ether. After the ether layer was washed with five 10-ml portions of water and dried over anhydrous magnesium sulfate, the solvent was removed *in vacuo* to afford the cyclopropenyl azide (0.815 g, 100%) as a colorless oil which crystallized upon refrigeration. Azide **6** is quite stable and has been stored neat in the crystalline state at about −10° for periods exceeding 6 months with no detectable decomposition. Purification, if necessary, may be effected by short-path distillation, pot temperature 40–50° (0.03–0.05 mm): mp ~2°; ν_{max} (CCl_4) 2950 (s), 2900 (m), 2870 (m), 2085 (vs), 1810 (w), 1475 (m), 1455 (m), 1390 (m), 1365 (m), 1258 (m), and 910 cm^{-1} (m); λ_{max} (cyclohexane) 295 nm (ϵ 28); mass spectrum *m/e* (rel intensity) 207 (33), 206 (11), 166 (23), 150 (16), 123 (68), 108 (10), 95 (18), 93 (10), 82 (10), 81 (15), 69 (18), 68 (15), 67 (23), 57 (100), 56 (10), 55 (23), 53 (12), 43 (27), 42 (38), 41 (29), and 39 (19).

Anal. Calcd for $C_{15}H_{27}N_3$: C, 72.24; H 10.91; N 16.85; mol wt, 249. Found: C, 72.36; H, 10.96; N, 16.74; mol wt, 250 (osmometric, CCl_4).

Reaction of azide **6** with potassium cyanide in aqueous acetonitrile followed by work-up as described above gave 1,2,3-tri-*tert*-butyl-3-cyanocyclopropene (80%), which was identical in all respects with an authentic sample prepared by the reaction of cation **5** with potassium cyanide: mp 30–31°; ν_{max} (CCl_4) 2970 (s), 2900 (m), 2870 (m), 2210 (m), 1845 (w), 1610 (w), 1475 (m), 1455 (m), 1380 (m), 1365 (m), and 1040 cm^{-1} (m); nmr (CCl_4) δ 1.00 (9 H, s) and 1.27 (18 H, s); mass spectrum *m/e* (rel intensity) 233 (4), 176 (100), 162 (13), 150 (19), 135 (12), 57 (72), and 41 (40).

Acknowledgments.—We thank the Italian National Research Council (C. N. R., Rome) and the Research Corporation for financial support of this research. We are also grateful to the Committee on International Exchange of Persons (Washington, D. C.) for a Senior Fulbright-Hays grant to J. C. (1972–1973) and for a travel grant to R. C. (summer, 1971).

Registry No.—**5**, 19985-80-9; **6**, 38409-72-2; 1,2,3-Tri-*tert*-butyl-3-cyanocyclopropene, 40893-42-3.

(24) (a) A. L. Van Geet, *Anal. Chem.*, **42**, 679 (1970); (b) *ibid.*, **40**, 2227 (1968).

Substituent Effects in the Ring Expansion Reactions of Isopropenylcycloalkanols by *tert*-Butyl Hypochlorite

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1-Isopropenylcyclobutanol was prepared by the conventional Grignard method. 1-Isopropenylcyclopropanol was synthesized by the addition of isopropenylmagnesium bromide to 1,3-dichloroacetone followed by ferric chloride induced coupling. The cyclobutanol underwent the chlorinative ring expansion with *tert*-butyl hypochlorite to produce 2-methyl-2-(chloromethyl)cyclopentanone in 81% yield. The cyclopropanol proved to be so labile that it spontaneously rearranged to 2,2-dimethylcyclobutanone. The acid-catalyzed ring expansion of 1-isopropenylcyclobutanol was accomplished with sulfuric acid in the presence of 2,4-dinitrophenylhydrazine. A slight preference for phenyl migration over methylene migration (60:40) was demonstrated in the reaction of 1-isopropenyl-1-indanol with *tert*-butyl hypochlorite. The substituent effect studies were extended to *trans*-1-isopropenyl-2-methylcyclopentan-1-ol and *exo*-2-isopropenylnorbornan-2-ol. Structure assignments for the ring expansion products from these two substrates were based on an nmr study. Methine carbon migration was shown to predominate over methylene carbon migration. These results were rationalized in terms of a nonconcerted mechanism with some carbonium-ion character in the transition state. The observed stereochemistry of the product ketones was explained on the basis of the conformational preference of the isopropenyl group in the reactant alcohol.

Part A

Carbocyclic ring expansion is a useful synthetic trick of the organic chemist.[1] Some of the classical methods applied to ring homologation by one carbon atom are the Demjanov[2] rearrangement, the Tiffeneau–Demjanov[2] rearrangement, and the pinacol[3] rearrangement. Well-known ring homologation methods which incorporate a heteroatom into the ring are the Baeyer–Villiger reaction (oxygen)[4] and the Beckmann rearrangement (nitrogen).[5] Several years ago we discovered a chlorinative ring-expansion reaction which homologates a ring by one carbon atom (eq 1).[6] This

(1) C. D. Gutsche and D. Redmore, "Carbocyclic Ring Expansion Reactions," Academic Press, New York, N. Y., 1968.

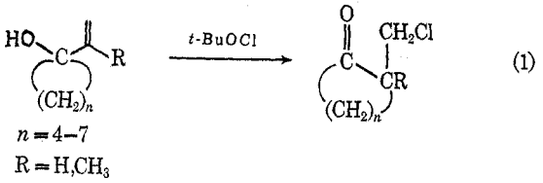
(2) P. A. Smith and D. R. Baer, "Organic Reactions," Vol. 11, Wiley, New York, N. Y., 1960, p 157.

(3) Y. Pocker in "Molecular Rearrangements," Part 1, P. de Mayo, Ed., Wiley, New York, N. Y., 1964, p 1.

(4) C. H. Hassall, "Organic Reactions," Vol. 9, Wiley, New York, N. Y., 1957, p 73.

(5) L. G. Donaruma and W. Z. Heldt, "Organic Reactions," Vol. 11, Wiley, New York, N. Y., 1960, p 1.

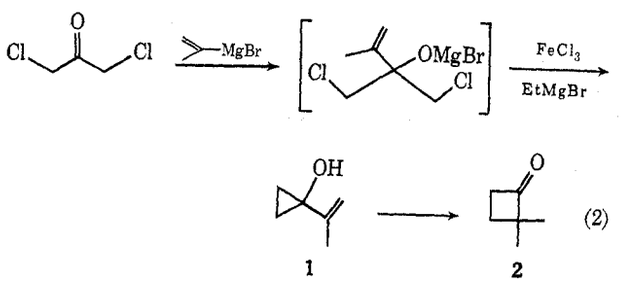
(6) C. R. Johnson, C. J. Cheer, and D. Goldsmith, *J. Org. Chem.*, **29**, 3320 (1964).



(1)

paper reports an investigation of the ring expansion of the smaller ring alcohols (eq 1, n = 2, 3) and a study of substituent effects and stereochemistry.

The synthesis of 1-isopropenylcyclopropanol was undertaken with the awareness that 1-vinylcyclopropanols were an unreported class of compound at the time, although several methods were available for the synthesis of 1-alkyl- and 1-arylcyclopropanols.[7] Reaction of 1,3-dichloroacetone with isopropenylmagnesium bromide, followed by addition of ferric chloride and ethylmagnesium bromide[8] and subsequent hydrolysis, gave, after removal of the solvent under vacuum and flash distillation under 20°, a 15% yield of a 4:1 mixture of 1-isopropenylcyclopropanol and 2,2-dimethylcyclobutanone (eq 2). Upon standing for 1



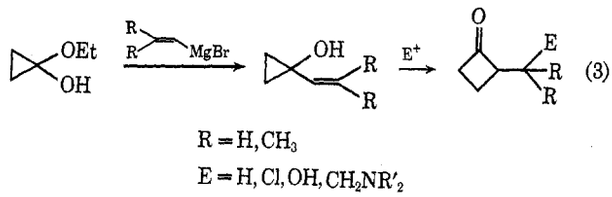
(2)

day at room temperature, either neat or in solution, the rearrangement of **1** to **2** was complete.

Reaction of the mixture of 1-isopropenylcyclopropanol and 2,2-dimethylcyclobutanone with *tert*-butyl hypochlorite resulted in a complex mixture of products, apparently owing to chlorination of 2,2-dimethylcyclobutanone competing with chlorinative ring expansion of the cyclopropanol. Although chlorinative ring expansion did occur, owing to the lack of synthetic utility of the reaction, the product was not rigorously characterized.

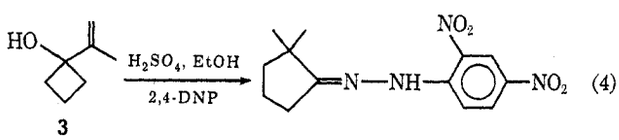
Several related vinylcyclopropanols have recently been reported. Wasserman and Clagett synthesized 1-cyclopentadienylcyclopropanol and found that it also undergoes a facile acid-catalyzed ring expansion.[9] Konzelman and Conley have reported isolating 1-vinylcyclopropanol as a minor product from the deamination of spiropentylamine.[10] Wasserman and coworkers have reported on the synthesis of two vinylcyclopropanols and their ring-expansion reactions with a variety of electrophilic reagents (eq 3).[11]

Attention was next focused on the cyclobutanol system. The synthesis of 1-isopropenylcyclobutanol was accomplished in 61% yield by Grignard addition to cyclobutanone. Because of the facility with which 1-



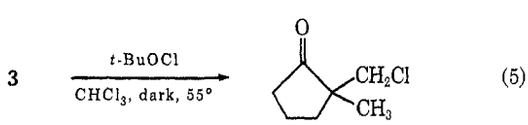
(3)

isopropenylcyclopropanol underwent acid-catalyzed ring expansion, efforts were made to bring about a similar reaction with isopropenylcyclobutanol. A variety of acids and solvents were examined with no success. No volatile ketonic product could be detected and dark, tarry residues resulted in most cases. However, a solution of 1-isopropenylcyclobutanol in ethanol and sulfuric acid in the presence of 2,4-dinitrophenylhydrazine resulted in a 51% yield of the hydrazone of 2,2-dimethylcyclopentanone (eq 4). When a similar



(4)

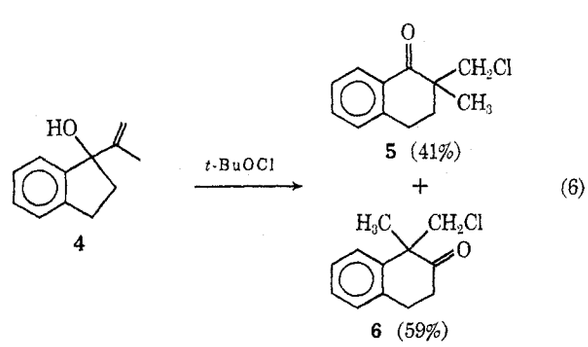
reaction was attempted with 1-isopropenylcyclopentanol, a dark solution resulted with no evidence of hydrazone formation. The reaction of 1-isopropenylcyclobutanol with *tert*-butyl hypochlorite resulted in an 81% yield of 2-(chloromethyl)-2-methylcyclopentanone (eq 5).



(5)

A study of substituent effects in the chlorinative ring expansion of 1-vinylcycloalkanols was initiated with the 1-indanol system. The synthesis of 1-isopropenyl-1-indanol (**4**) was accomplished in 38% yield by the Grignard reaction on 1-indanone.

The usual procedure[6] for the chlorinative ring expansion on 1-isopropenyl-1-indanol resulted in an 88% yield of product consisting of two isomers (eq 6). The



(6)

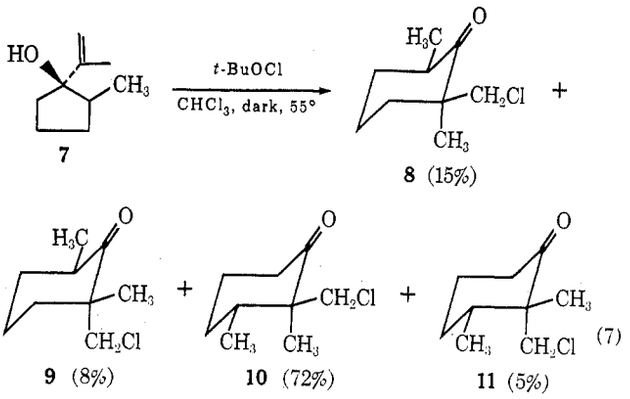
isomers were separated and collected by glc and identified through their infrared and nmr spectra. The first isomer eluted exhibited a carbonyl band at 1680 cm^{-1} and was assigned the 1-tetralone structure **5**. The second isomer showed a carbonyl band at 1720 cm^{-1} and was assigned the 2-tetralone structure **6**.

Alcohol **7** was prepared by the addition of isopropenylmagnesium bromide to 2-methylcyclopentanone. The Grignard reaction was accomplished in 28% yield, although the actual yield based on consumed starting

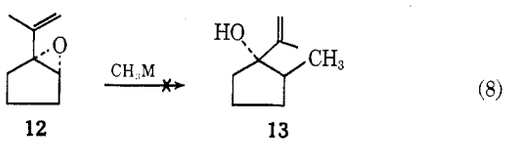
(7) C. H. DePuy, *Trans. N. Y. Acad. Sci., Ser. II*, **28**, 561 (1966).
(8) C. H. DePuy, G. M. Dappen, K. L. Eilers, and R. A. Klein, *J. Org. Chem.*, **29**, 2813 (1964).
(9) H. H. Wasserman and D. C. Clagett, *J. Amer. Chem. Soc.*, **88**, 5368 (1966).
(10) L. M. Konzelman and R. T. Conley, *J. Org. Chem.*, **33**, 3828 (1968).
(11) H. H. Wasserman, R. E. Cochoy, and M. S. Baird, *J. Amer. Chem. Soc.*, **91**, 2375 (1969).

material would be higher since a considerable amount of 2-methylcyclopentanone was recovered. Two isomers are theoretically possible from the Grignard addition, but glc analysis with several columns under varying conditions showed only one peak. Literature data on related reactions supports the structure **7** having trans alkyl groups.[12]

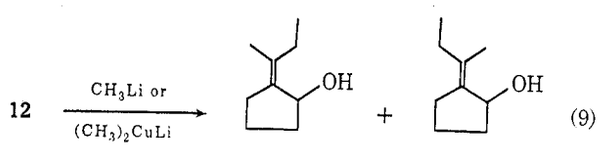
Following reaction of the alcohol **7** with *tert*-butyl hypochlorite and removal of the solvent, the infrared spectrum of the crude product showed a strong carbonyl band at 1720 cm^{-1}. Glc analysis showed the presence of four isomers in the ratio 15:8:72:5 (eq 7).



A key step in one scheme planned for the synthesis of *cis*-1-isopropenyl-2-methylcyclopentan-1-ol (**13**) was the addition of an organometallic reagent to the oxirane moiety of 1-isopropenyl-1,2-epoxycyclopentane (**12**) (eq 8). Neither the addition of methyllithium or

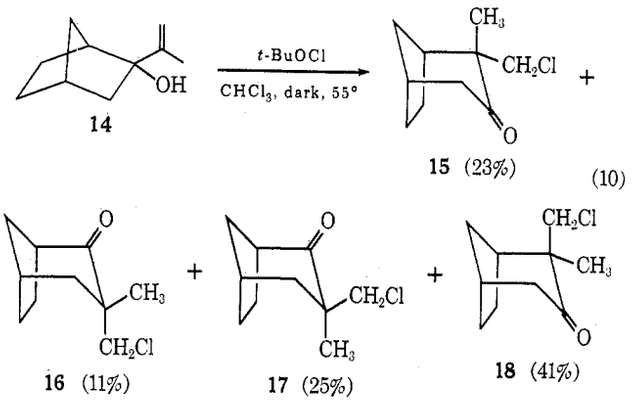


lithium dimethylcuprate yielded the desired product, but rather gave a mixture of isomeric alcohols resulting from conjugate addition (eq 9). The facile reac-



tion observed in this case with the cuprate initiated our interest in exploring the general reactions of cuprates and epoxides.

The reaction of isopropenylmagnesium bromide with bicyclo[2.2.1]heptan-2-one gave 2-isopropenylbicyclo[2.2.1]heptan-2-ol (2-isopropenylnorbornan-2-ol) (**14**) in 82% yield. Only one isomer could be detected by glc analysis. The product was assigned the exo-alkyl configuration by analogy with the addition of methylmagnesium iodide to 2-norbornanone, where 95% of the *exo*-2-methylnorbornan-2-ol was obtained.[13] When subjected to the chlorinative ring expansion reaction, *exo*-2-isopropenylnorbornan-2-ol (**14**) gave a mixture of four isomeric ketones (eq 10).



In the chlorinative ring expansion of **4** it is observed that phenyl migration is slightly preferred over methylene, and in the ring expansions of **7** and **14** it is found that methine migration is preferred to methylene. These observations are consistent with rearrangements involving carbonium ion intermediates. Migratory preferences involving cyclic systems never tend to be as clear-cut as those involving acyclic systems because of the arrogation of electronic factors by steric effects.[1]

Part B

Structural Assignments by Nmr Studies.—Aromatic solvent induced shifts (ASIS) in nmr spectra have been documented for many different classes of compounds.[14] Ketones, and in particular methyl-substituted cyclohexanones, have been studied extensively. The empirical generalization of Connolly and McCrindle for predicting the direction and magnitude of benzene-induced solvent shifts[14,15] was especially useful. This rule states that, if a reference plane (P) is drawn through the carbon of the carbonyl group at right angles to the carbon–oxygen bond, then protons close to P show no shift or very small shifts; protons in front of P, *i.e.*, on the same side as the oxygen of the carbonyl group, are deshielded; while protons behind P are shielded. Some data selected from the literature[15,16] on ASIS of methyl-substituted cyclohexanones are summarized as follows.

Methyl substituent	$\Delta^{CDCl_3}_{C_6H_6}$, Hz
2-CH_3 eq	−1.6 to +3.0
2-CH_3 ax	+16.6 to +18.0
3-CH_3 eq	+18.5 to +21.2
3-CH_3 ax	+11.8

Another empirical generalization which has proved useful in distinguishing the axial and equatorial members of isomer pairs is the observation that an axial 2-methyl substituent in a cyclohexanone gives a signal downfield from an equatorial 2-methyl sub-

(12) J. P. Battioni, W. Chodkiewicz, and P. Cadiot, *C. R. Acad. Sci., Ser. C*, **264**, 991 (1967).

(13) N. J. Tiovonen and P. J. Malkonen, *Suom. Kemistilehti*, **32**, 277 (1959).

(14) (a) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, New York, N. Y., 1969, pp 104–113, 246; (b) N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, San Francisco, Calif., 1964.

(15) J. D. Connolly and R. McCrindle, *Chem. Ind. (London)*, 379 (1965).

(16) M. Fetzion, J. Gore, P. Laszlo, and B. Waegell, *J. Org. Chem.*, **31**, 4047 (1966).

stituent in its nmr spectrum run in deuteriochloroform solution.[14b,16,17]

The pertinent nmr data for the four isomers from the ring expanison of **7** necessary for structure assignments based on these two empirical rules are given in Table I. The solvent shift values for the methyl

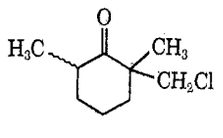
TABLE I

NMR DATA FOR THE CYCLOHEXANONE ISOMERS FROM THE RING EXPANSION OF *trans*-1-ISOPROPENYL-2-METHYLCYCLOPENTAN-1-OL[a,d]

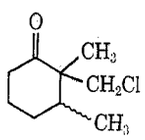
Isomer		ν_{CDCl_3}, Hz	$\nu_{C_6H_6}$, Hz	$\Delta^{CDCl_3}_{C_6H_6}$, Hz[b]
A	CH_3 (d)	61 (J = 6)	55 (J = 6)	6
(15%)	CH_3 (s)	76	53	23
	CH_2Cl[c]	218 (J_{AB} = 0)	212 (J_{AB} = 0)	6
	$\Delta\nu_{AB}$	0	0	
B	CH_3 (d)	62 (J = 6)	57 (J = 6)	5
(8%)	CH_3 (s)	69	65	4
	CH_2Cl	222 (J_{AB} = 11)	194 (J_{AB} = 11)	28
	$\Delta\nu_{AB}$	14	12	
C	CH_3 (d)	55 (J = 6)	36 (J = 7)	19
(72%)	CH_3 (s)	76	65	11
	CH_2Cl	222 (J_{AB} = 11)	210 (J_{AB} = 11)	12
	$\Delta\nu_{AB}$	10	9	
D	CH_3 (d)	57 (J = 6)	36 (J = 6)	21
(5%)	CH_3 (s)	63	37	26
	CH_2Cl	221 (J_{AB} = 11)	207 (J_{AB} = 11)	14
	$\Delta\nu_{AB}$	30	44	

[a] Spectra were run on a 60-MHz instrument (Varian A-60A) with the compounds in 10% w/w solution. [b] The $\Delta^{CDCl_3}_{C_6H_6}$ values for the chloromethyl groups are included in the table, but their significance must be interpreted with caution since $\Delta\nu_{AB}$ is observed to vary with solvent. Although this phenomenon has been observed previously (ref 14a, p 144), the precise solvent effect (if any) on rotamer populations cannot be predicted. [c] The protons of the chloromethyl group in these compounds are chemically nonequivalent (since the methylene group is attached to an asymmetric carbon) and can be magnetically equivalent resulting in an A_2 singlet (isomer A) or magnetically nonequivalent resulting in an AB quartet (isomers B, C, D). [d] Chemical shift values are expressed in hertz downfield from TMS. J's are in hertz.

doublets show unambiguously that A and B are the 6-methyl isomers and that C and D are the 3-methyl isomers.



A and B



C and D

Analysis of the solvent shift data for the methyl singlets (2-CH_3) indicates the following conformational assignments. Interpretation of the chemical-shift data

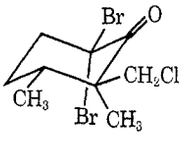
	Isomer	$\Delta^{CDCl_3}_{C_6H_6}$, Hz	2-CH_3 Conformation
6-CH_3	A	23	ax
	B	4	eq
3-CH_3	C	11	eq
	D	26	ax

for the 2-methyl singlets in deuteriochloroform based on the rule that axial methyls appear at lower field than equatorial methyls indicates the following conformational assignments.

	Isomer	ν_{CDCl_3}, Hz	2-CH_3 Conformation
6-CH_3	A	76	ax
	B	69	eq
3-CH_3	C	76	ax
	D	63	eq

Both types of data are in agreement for isomers A and B, which can now be assigned as **8** and **9**, respectively. However, note that the two methods yield contradictory assignments for C and D.

We have solved this dilemma by a study modeled after the work of Wolinsky on the pmr spectra of brominated bicyclooctanes.[18] Wolinsky found that a bromine in 1,3-diaxial relationship to a methyl group will shift the methyl signal about 20 Hz to lower field, while a bromine and methyl in a 1,3-diequatorial relationship cause a much smaller downfield shift (~8 Hz) of the methyl signal. Isomer C was dibrominated and the nmr spectrum of the product was obtained. The 2-methyl singlet of the dibromo ketone occurred at 18 Hz lower field than in C while the chloromethyl experienced an average downfield shift of only 12 Hz.[19] We interpret this to mean that the dibromo ketone has the structure shown as **19** and hence isomer C has structure **10**, leaving structure **11** for isomer D.



19

The mixture, obtained from chlorination of **14**, was separated into its components by preparative glc and nmr data obtained (Table II). For this mixture

TABLE II

NMR DATA FOR THE BICYCLOOCTANONE ISOMERS FROM THE RING EXPANSION OF *exo*-2-ISOPROPENYLNORBORNAN-2-OL[a,e]

Isomer		ν_{CDCl_3}, Hz	$\nu_{C_6H_6}$, Hz	$\Delta^{CDCl_3}_{C_6H_6}$, Hz[b]
15	CH_3	76	62[d]	14
	CH_2Cl[c]	222 (J_{AB} = 11)	222 (J_{AB} = 11)	0
	$\Delta\nu_{AB}$	7	9	
16	CH_3	70	58	12
	CH_2Cl	207 (J_{AB} = 11)	196 (J_{AB} = 11)	11
	$\Delta\nu_{AB}$	31	37	
17	CH_3	72	56	16
	CH_2Cl	206 (J_{AB} = 11)	197 (J_{AB} = 11)	9
	$\Delta\nu_{AB}$	43	51	
18	CH_3	68	66	2
	CH_2Cl	216 (J_{AB} = 11)	197 (J_{AB} = 11)	19
	$\Delta\nu_{AB}$	11	9	

[a] Spectra were run on a 60-MHz instrument (Varian A-60A) with the compounds in 25% w/w solution. [b] See footnote *b*, Table I. [c] AB quartets are observed for all four of the bicyclooctanone isomers. See footnote *c*, Table I. [d] CH_3 (d), J = 0.7 Hz. [e] Chemical shift values are expressed in hertz downfield from TMS. J's are in hertz.

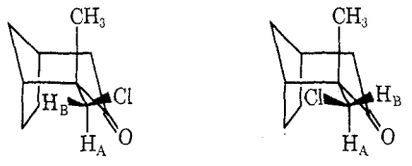
(17) F. Johnson, N. A. Starkovsky, and W. D. Gurowitz, *J. Amer. Chem. Soc.*, **87**, 3492 (1965).

(18) J. Wolinsky, *J. Org. Chem.*, **26**, 704 (1961).

(19) The methylene of the chloromethyl appears as an AB quartet, so the problem is complicated, but a more detailed analysis has led us to the same conclusion.

of bicyclooctanones nmr integration of the α-carbonyl protons should serve to distinguish the 2-keto and 3-keto isomer pairs. This proved to be the case. The structures of the individual isomers of each pair were then assigned using the first two methods as previously employed for the cyclohexanones. Unlike the data for the cyclohexanones, the two methods arrived at the same assignments for the bicyclooctanone mixture.

The methyl doublet (J = 0.7 Hz) observed for isomer **15** was attributed to long-range coupling of the W type[20] with one of the chloromethyl protons. Although the coupling constant could not be measured, the coupling was observed to occur with H_A (the higher field proton; 218 Hz) as evidenced by broadening and fine splitting of the two lines for H_A. There are two conformers (**20** and **21**) of **15** which have the correct



20 **21**

geometry to give the observed long-range W type coupling. Assuming that the conformational preference will be the same in deuteriochloroform and benzene, the preferred conformer can then be assigned from the solvent shift data for H_A and H_B. Conformer **20** has H_A and H_B in different environments with respect to the solvent-shift plane (P) and H_A is predicted to undergo no shift while H_B is expected to undergo a fairly large upfield shift. Conformer **21**, on the other hand, has H_A and H_B both in the solvent-shift plane (P), and no solvent shift is expected for either. Since no solvent shift is observed for either

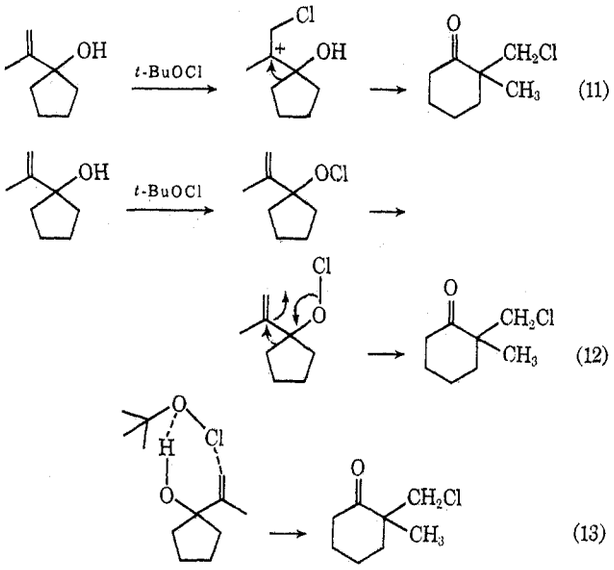
	ν_{CHCl_3}, Hz	$\nu_{C_6H_6}$, Hz	$\Delta^{CDCl_3}_{C_6H_6}$, Hz
H_A	218	218	0
H_B	226	226	0

H_A and H_B, conformer **21** is believed to be the preferred conformer.

Stereochemistry and Mechanism.—In eq 7 and 10 it is shown that methine migration is preferred over methylene migration in these chlorinative ring-expansion reactions. Examination of the product distribution for the two reactions also shows that there is a definite configurational preference for the chloromethyl group in the product ketones. In the cyclopentanol **7** the isopropenyl group is trans to the methyl, and, if the norbornyl system is viewed as a substituted cyclopentane, then the isopropenyl group of the norbornanol **14** is trans to the ethano bridge. The configuration of the chloromethyl in the product ketones can then be consistently correlated with the geometry of both isopropenyl alcohols. The important factor is the trans–cis relationship of the chloromethyl group in the ketones to the alkyl group which corresponds to the 2-alkyl substituent in the alcohol. For the cyclohexanones this is the relationship of the chloromethyl to the 3- and 6-methyl substituents, and for the bicyclooctanones it is the relationship of the chloromethyl to the ethano bridge. The product distribution data for the two reactions can then be illustrated as follows, with the trans–cis ratio given for each isomer pair. No significance can be attached to the trans–cis ratio for the pair of 6-methylcyclohexanones, as isomerization may have occurred during the glc analysis. However, isomerization is not possible for the other three isomer pairs.

Isomer pair	Trans:cis ratio for the chloromethyl–alkyl group relationship
3-Methylcyclohexanones	14.4:1
2-Bicyclooctanones	2.3:1
3-Bicyclooctanones	1.8:1

Three mechanisms have been proposed for the chlorinative ring expansion with *tert*-butyl hypochlorite.[6] They are (1) electrophilic attack on the olefin by *tert*-butyl hypochlorite to generate an intermediate carbonium ion followed by an alkyl shift and collapse to product (intermolecular) (eq 11); (2) hypochlorite ester interchange followed by intramolecular reorganization (eq 12); and (3) a cyclic, concerted mechanism (eq 13).

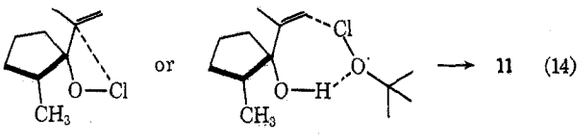


(11)

(12)

(13)

The observation that in these chlorinative ring-expansion reactions methine carbon migration is preferred over methylene is consistent with that expected of a ring-expansion reaction with some cationic character in the transition state (eq 11). Mechanisms 12 and 13 involve a concerted step, thus requiring that the isopropenyl group be in the conformation with the methyl over the face of the ring, thereby predicting **11** as the major product (eq 14), contrary to what is observed (eq 7).

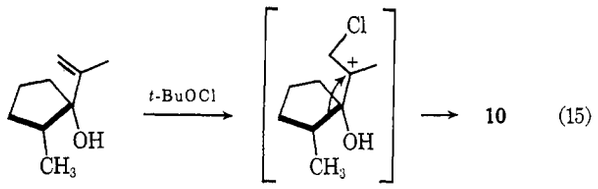


(14)

The evidence thus points to a nonconcerted mechanism with some carbonium ion character in the transition state. Additionally, a preferred mechanism must account for the observed trans–cis ratio in the 3-methylcyclohexanone isomer pair. Inspection of

(20) Reference 14a, pp 334–341.

Dreiding models and Hirschfelder models indicates that the preferred conformation for *trans*-1-isopropenyl-2-methylcyclopentan-1-ol is the one with the methylene carbon situated over the face of the cyclopentane ring. If electrophilic attack by *tert*-butyl hypochlorite in this conformation (**22**) is then assumed, followed by a rapid alkyl shift to the intermediate "carbonium ion," the product predicted would be **10**, as is actually observed (eq 15). An additional requirement for



22

obtaining the observed trans-cis ratio (14.4:1) is that the alkyl shift occurs before rotational equilibration of the carbonium ion can take place. The mechanism of eq 15 seems to best explain the observed product distribution from the chlorinative ring expansion of *trans*-1-isopropenyl-2-methylcyclopentan-1-ol. The mechanistic arguments applied to the 2-methylcyclopentanol system can be applied to *exo*-2-isopropenylnorbornan-2-ol as well.

Experimental Section

Infrared spectra were obtained on a Perkin-Elmer 137 B spectrophotometer. The nmr spectra were taken on either a Varian A-60A or Varian T-60 spectrometer with tetramethylsilane (TMS) as the internal standard. The sweep width was 500 Hz, unless otherwise indicated. The glc work was performed with a Hewlett-Packard 5750 and Prepmaster, Jr.

All Grignard reactions were run under a dry nitrogen atmosphere. Grignard solvents (ether and tetrahydrofuran) were dried by distillation from sodium dispersion.

The melting points and boiling points are uncorrected. Elemental analyses were performed by Midwest Microlab, Inc., Indianapolis, Ind.

1-Isopropenylcyclopropanol (1).—To 2.68 g (0.11 mol) of magnesium turnings in 20 ml of tetrahydrofuran (THF) there was added dropwise over 45 min a solution of 10.65 ml (14.5 g, 0.12 mol) of 2-bromopropene in 80 ml of THF. The temperature was maintained at 40–50° throughout the addition, and stirring was continued for 30 min after the addition was complete. The solution of isopropenylmagnesium bromide was then cooled to −40° and a solution of 12.70 g (0.10 mol) of 1,3-dichloroacetone (Eastman) in 100 ml of THF was added over a 1-hr period with the temperature maintained at −40°. Stirring was continued for 30 min at −40° and for 3 hr longer, during which time the temperature was allowed to rise to 0°. There was then added simultaneously over a 1.5-hr period 400 ml of an ether solution containing 0.6 mol of ethylmagnesium bromide and a solution of 1.3 g (0.008 mol) of anhydrous ferric chloride in 100 ml of THF. The reaction mixture was allowed to stir for an additional 6 hr at 0°, followed by hydrolysis at 0° with a phosphate buffer solution (pH 7.0). The precipitated salts were filtered, and the filtrate was dried over anhydrous sodium sulfate. The solvent was removed under vacuum with a maximum pot temperature of 20° allowed. The residue was flash distilled with the pot temperature maintained under 20° to give 1.483 g (15%) of a clear, colorless liquid. The infrared spectrum of the product showed a strong hydroxyl band at 3300 cm^{-1} and absorptions at 3020, 1640, and 880 cm^{-1}. In addition, there was a medium band at 1770 cm^{-1}. The nmr spectrum of the product revealed the presence of two compounds in a 4:1 ratio. There was a complex multiplet of the AA'BB' type centered at δ 0.78 (cyclopropyl H), a quartet at 1.67 (isopropenyl $-CH_3$), a singlet at 3.88 (–OH), and two multiplets at 4.75 and 4.93 (vinyl H of isopropenyl group). These resonances were attributed to 1-isopropenylcyclopropanol. In addition, there was a singlet at δ 1.13 (*gem*-dimethyl), a triplet at 1.67 (β methylene H), and a triplet at 1.87 (α methylene H). These resonances were attributed to 2,2-dimethylcyclobutanone. Although the 1-isopropenylcyclopropanol was the major component initially, there was a slow conversion to 2,2-dimethylcyclobutanone which was complete after 24 hr as evidenced by the nmr spectrum. This rearrangement occurred either in carbon tetrachloride or neat. The 2,2-dimethylcyclobutanone was converted to its **2,4-dinitrophenylhydrazone** (recrystallized from 95% ethanol), mp 139–140° (lit.[21] mp 140–141°).

Anal. Calcd for $C_{12}H_{14}N_4O_4$: C, 51.79; H, 5.08. Found: C, 51.64; H, 5.02.

1-Isopropenylcyclobutan-1-ol (**3**).—To 4.38 g (0.18 mol) of magnesium turnings in 30 ml of tetrahydrofuran (THF) there was added 16.9 g (0.09 mol) of 1,2-dibromoethane in 120 ml of THF. The addition was carried out over a 1.25-hr period with the temperature maintained at 50°. After the solution was stirred for an additional 30 min, 12.35 g (0.102 mol) of 2-bromopropene (Columbia Organics, 99+% purity) in 65 ml of THF was added to the reaction mixture over a 1.5-hr period. Stirring was continued for 45 min with the temperature maintained at 45° throughout the entire 2.25-hr period.

A solution of 4.2 g (0.06 mol) of cyclobutanone (Columbia Organics) in 40 ml of THF was added over a 1.25-hr period to the Grignard solution maintained at 50°. Stirring was continued for 15 hr at 50°. The reaction mixture was then cooled with an ice bath and hydrolyzed by the dropwise addition of saturated ammonium chloride solution. The THF solution was decanted from the precipitated salts and the precipitate was washed with three 100-ml portions of ether. The combined THF–ether solution was washed with two 100-ml portions of water and 100 ml of saturated sodium chloride solution. The combined water washings were extracted with 100 ml of ether; the THF–ether solution was washed once more with 100 ml of saturated sodium chloride solution and dried over anhydrous sodium sulfate. The ether and THF were removed by distillation at atmospheric pressure with the last traces removed by distillation at 60 mm (water pump). The viscous, yellow residue was flash distilled at 1 mm to give a clear, colorless liquid, which was distilled through a 4-cm column to yield 4.11 g (61%) of 1-isopropenylcyclobutan-1-ol: bp 48–50° (7.8 mm); $n^{25}D$ 1.4633; ir (film) 3350 (s, –OH), 3100 (w, $=CH_2$), 2950 (s, –CH), 1650 (m, $>C=CH_2$), 900 cm^{-1} (s, $>C=CH_2$); nmr (CCl_4) δ 1.77 (m, $-CH_3$), 2.10 (m, $-CH_2-$), 3.42 (s, –OH), 4.78 (m, trans vinyl H), 4.93 (m, cis vinyl H).

Anal. Calcd for $C_7H_{12}O$: C, 74.94; H, 10.80. Found: C, 74.83; H, 10.74.

Acid-Catalyzed Rearrangement of 1-Isopropenylcyclobutan-1-ol.—To 20 ml of 0.15 *M* 2,4-dinitrophenylhydrazine reagent was added 119.2 mg (1 mmol) of 1-isopropenylcyclobutan-1-ol. The solution was allowed to stand at room temperature for 3 days, during which period the 2,4-dinitrophenylhydrazone slowly crystallized as long, fine needles. The product was collected by filtration and dried to yield 149 mg (51%) of product, mp 142–143°. The 2,4-dinitrophenylhydrazone (recrystallized once from 95% ethanol) had mp 142–143° (lit.[22] mp 144°).

2-Methyl-2-(chloromethyl)cyclopentanone.—A solution of 1-isopropenylcyclobutan-1-ol (0.4475 g, 0.004 mmol) in 20 ml of alcohol-free chloroform was heated to 55° in a black-painted flask fitted with a reflux condenser. To the stirred solution was added 0.476 ml (0.434 g, 0.004 mol) of *tert*-butyl hypochlorite.[23] The reaction was completed in 2 hr as evidenced by a negative test for *tert*-butyl hypochlorite with potassium iodide–starch test paper. The chloroform solution was passed through a short column of alumina, and the chloroform was removed by distillation at atmospheric pressure. The pale-yellow liquid residue was distilled twice with a short-path apparatus to yield 0.4281g (73%) of 2-methyl-2-(chloromethyl)cyclopentanone: bp 46–48° (1.8 mm); $n^{25}D$ 1.4663; ir (film) 2950 (m, –CH), 1740 (s, C=O), 740 (m, –CCl); nmr (CCl_4) δ 1.05 (s, $-CH_3$), 2.08 (broad m, $-CH_2-$), 3.46 (AB quartet, J = 11 Hz, $-CH_2Cl$).

Anal. Calcd for $C_7H_{11}OCl$: C, 57.33; H, 7.56. Found: C, 57.21; H, 7.46.

Reaction of 1-Isopropenyl-1-indanol (**4**) **with *tert*-Butyl Hypochlorite.**—To a magnetically stirred solution of 0.3485 g (2

(21) H. Bestian and D. Guenther, *Angew. Chem.*, **75**, 841 (1963).

(22) C. F. Wilcox, Jr., and M. Mesirov, *J. Org. Chem.*, **25**, 1841 (1960).

(23) D. J. Pasto and C. R. Johnson, "Organic Structure Determination," Prentice-Hall, Englewood Cliffs, N. J., 1969, p 363.

mmol) of 1-isopropenyl-1-indanol[24] in 10 ml of alcohol-free chloroform in a black-painted flask at 55° was added 0.24 ml (0.217 g, 2 mmol) of freshly prepared *tert*-butyl hypochlorite.[23] After complete reaction (38.5 hr, negative potassium iodide–starch test) the solvent was removed *in vacuo*. The viscous, yellow residue (0.411 g) was subjected to infrared and glc analysis. The infrared spectrum of this material contained carbonyl bands at 1720 and 1680 cm^{-1}, with the more intense band at 1720 cm^{-1}. Glc analysis was carried out with a 8 ft × 0.25 in., 20% diethylene glycol succinate on Chromosorb W, 60–80 mesh column at a column temperature of 172° and a helium flow of 150 ml/min. The chromatogram revealed three peaks with retention times of 19 (minor), 33 (major), and 39.5 min (major). The minor peak at 19 min was not identified, and planimetric integration showed it to be 11% of the total mixture. Based on glc analysis, the yield of tetralones was 0.266 g (88%). Planimetric integration of the two major peaks at 33 (isomer **5**) and 39.5 min (isomer **6**) gave a ratio of 41:59. Collection of the two peaks by glc and their infrared spectra and elemental analyses gave the following data. Isomer **5** had ir (CCl_4) 1680 cm^{-1}. *Anal.* Calcd for $C_{12}H_{13}OCl$: C, 69.06; H, 6.29. Found C, 68.78; H, 6.15. Isomer **6** had ir (CCl_4) 1720 cm^{-1}. *Anal.* Calcd for $C_{12}H_{13}OCl$: C, 69.06; H, 6.29. Found: C, 68.93; H, 6.21.

***trans*-1-Isopropenyl-2-methylcyclopentan-1-ol (7).**—to 7.3 g (0.30 mol) of magnesium turnings (Fisher, Laboratory Reagent) in tetrahydrofuran (THF) was added, dropwise with stirring, 13.0 ml (28.2 g, 0.15 mol) of 1,2-dibromoethane in 200 ml of THF over a period of 2 hr while the temperature was maintained at 50°. After stirring for an additional 30 min at 50°, 15.1 ml (20.6 g, 0.17 mol) of 2-bromopropene (Columbia Organics, 99+% purity) in 110 ml of THF was added over a period of 1.5 hr with the temperature maintained at 45°. The stirring was continued at 45° for 30 min after the addition was completed.

A solution of 9.814 g (0.10 mol) of 2-methylcyclopentanone[25] in 70 ml of THF was added to the Grignard solution at 50° over a 2.5-hr period. Stirring was continued for 14 hr with the reaction temperature maintained at 50° throughout. The reaction mixture was cooled with an ice bath, hydrolyzed, and worked up as described for the preparation of 1-isopropenyl cyclobutan-1-ol. The product was fractionally distilled through a 20-cm Podbielniak column to yield 3.90 g (28%) of pure *trans*-1-isopropenyl-2-methylcyclopentan-1-ol: bp 62° (9.2 mm); $n^{25}D$ 1.4692; ir (neat) 3400 (m, –OH), 2825 (m), 1650 (m, $=CH_2$), 950 (m), 900 cm^{-1} (m); nmr (CCl_4) δ 0.83 (d, J = 6 Hz, $-CH_3$), 1.70 (m, $-CCH_3$), 1.70 (m, $-CH_2-$), 4.82 (m, trans vinyl H), 5.02 (m, cis vinyl H).

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 76.84; H, 11.35.

Reaction of *trans*-1-Isopropenyl-2-methylcyclopentan-1-ol with *tert*-Butyl Hypochlorite.—To a magnetically stirred solution of 1.05 g (7.5 mmol) of *trans*-1-isopropenyl-2-methylcyclopentan-1-ol in 40 ml of alcohol-free chloroform in a black-painted flask at 55° was added 0.92 ml (0.84 g, 7.7 mmol) of freshly prepared *tert*-butyl hypochlorite.[23] After completion of the reaction (8 hr, negative potassium iodide–starch test) the solvent was removed *in vacuo* to leave 1.29 g of a clear, yellow oil. The infrared spectrum of this material had a strong carbonyl band at 1720 cm^{-1}. Glc analysis was performed with a 16 ft × 0.25 in., 20% diethylene glycol succinate on Chromosorb W, 60–80 mesh column, with a column temperature of 180° and a helium flow of 46 ml/min. The chromatogram revealed at least 15 minor peaks with retention times in the range 0–13 min, and four major peaks with retention times of 16 (isomer A), 20 (isomer B), 25 (isomer C), and 29.5 min (isomer D). Planimetric integration gave the following percentages for the total of the four major peaks: isomer A, 15%; isomer B, 8%; isomer C, 72%; and isomer D, 5%. No attempt was made to identify any of the minor peaks in the 0–13 min range. The four major peaks were collected with a 20 ft × 0.375 in., 20% diethylene glycol succinate on Chromosorb W, 60–80 mesh column. Temperature programming was employed with a postinjection interval of 20 min at 145°, a programmed increase of 2°/min to 188°, and an additional 20 min at the upper limit of 188°. The helium flow rate was 150 ml/min, and the total time of the cycle was 54 min. Nmr data in deuteriochloroform and benzene were collected for all four isomers (Table I). An elemental analysis was obtained for isomer C.

Anal. Calcd for $C_9H_{15}OCl$: C, 61.88; H, 8.67. Found: C, 61.72; H, 8.73.

***exo*-2-Isopropenyl-2-norbornanol (14).**—The procedure was identical with that used for the preparation of *trans*-1-isopropenyl-2-methylcyclopentan-1-ol. A 19.83-g (0.18 mol) portion of 2-norbornanone was allowed to react, with all other reagents scaled up accordingly. After the usual work-up, distillation through a Vigreux column yielded 22.58 g (82%) of *exo*-2-isopropenyl-2-norbornanol: bp 49–51° (0.8 mm); ir (film) 3600, 3450, 1650, 900 cm^{-1}; nmr (CCl_4) δ 1.80 (m, $-CCH_3$), 4.78 (m, trans vinyl H), 4.92 (m, cis vinyl H).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.60. Found: C, 78.92; H, 10.61.

Reaction of *exo*-2-Isopropenyl-2-norbornanol with *tert*-Butyl Hypochlorite.—To a magnetically stirred solution of 3.81 g (25 mmol) of *exo*-2-isopropenyl-2-norbornanol in 125 ml of alcohol-free chloroform was added 3.10 ml (2.82 g, 26 mmol) of freshly prepared *tert*-butyl hypochlorite.[23] After completion of the reaction (8 hr, negative potassium iodide–starch test), the solvent was removed *in vacuo* to leave 4.46 g of a clear, yellow oil. The infrared spectrum of this material had a strong carbonyl band at 1700 cm^{-1}. Glc analysis was carried out with a 16 ft × 0.25 in., 10% ethylene glycol succinate on Chromosorb W, 60–80 mesh column with a column temperature of 150° and a helium flow rate of 60 ml/min. The chromatogram showed two very minor peaks at 18–20 min and four major peaks at 27 (isomer **15**), 30 (isomer **16**), 34 (isomer **17**), and 38 min (isomer **18**). Planimetric integration gave the following percentages for the four major peaks: isomer **15**, 23%; isomer **16**, 11%; isomer **17**, 25%; and isomer **18**, 41%. The four major peaks were collected by preparative glc using a 6 ft × 0.75 in., 20% diethylene glycol succinate on Chromosorb W, 10–60 mesh column, with a 150° column temperature and a nitrogen flow rate of 300 ml/min. Four fractions were collected corresponding to each of the four peaks. The first and the fourth fractions contained over 75% of the desired isomer and were further purified by a second pass through the 6 ft × 0.75 in. column. The second and third fractions were about 50:50 mixtures of the desired isomers and they were further purified by collecting from a 25 ft × 0.375 in., 15% ethylene glycol succinate on Chromosorb W, 60–80 mesh column, at 170° column temperature and a nitrogen flow rate of 100 ml/min. Nmr data in deuteriochloroform and benzene were obtained for the four isomers (Table II). An elemental analysis was obtained for isomer **18**.

Anal. Calcd for $C_{10}H_{15}OCl$: C, 64.33; H, 8.11. Found: C, 64.18; H, 8.09.

Registry No.—**1**, 40791-85-3; **2**, 1192-14-9; **2** DNP, 4070-16-0; **3**, 40791-88-6; **4**, 19063-65-1; **5**, 40791-90-0; **6**, 40791-91-1; **7**, 40791-92-2; **8**, 40791-93-3; **9**, 40791-94-4; **10**, 40791-95-5; **11**, 40791-96-6; **14**, 40791-97-7; **15**, 40791-98-8; **16**, 40791-99-9; **17**, 40792-00-5; **18**, 40792-01-6; *tert*-butyl hypochlorite, 507-40-4; 2-bromopropene, 557-93-7; 1,2-dibromoethane, 106-93-4; cyclobutanone, 1191-95-3; 2,2-dimethylcyclopentanone, 4541-32-6; 2-methyl-2-(chloromethyl)cyclopentanone, 40792-02-7; 2-methylcyclopentanone, 1120-72-5; 2-norbornanone, 497-38-1.

(24) C. J. Cheer and C. R. Johnson, *J. Amer. Chem. Soc.*, **90**, 178 (1968).

(25) The 2-methylcyclopentanone was prepared from 1-methylcyclopentene by the hydroboration–dichromate oxidation procedure of H. C. Brown and C. P. Garg, *J. Amer. Chem. Soc.*, **83**, 2544 (1961).