The Reaction of Norbornene with *t*-Butyl Hypochlorite and the Stereoisomeric 2,3-Chlorohydroxybicyclo[2.2.1]heptanes

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The action of *t*-butyl hypochlorite on norbornene under free-radical conditions results primarily in the formation of the *trans* adduct. In addition, the reaction yields chlorination (substitution) products and some of the *cis* adduct. Ether cleavage of the adducts affords the corresponding 2,3-chlorohydrins. Oxidation of the *trans* chlorohydrin yields 3-*endo*-chlorobicyclo[2.2.1]heptan-2-one, which upon reduction with sodium borohydride gives the *endo*-*cis*-chlorohydrin. Chlorination of norcamphor produces 3-*exo*-chlorobicyclo[2.2.1]heptan-2-one from which the *exo*-*cis*-chlorohydrin is obtained by sodium borohydride reduction.

The reaction of *t*-butyl hypochlorite with olefins in polar solvents generally results in electrophilic addition. With dienes, such as butadiene and isoprene, 1,2-addition usually predominates over 1,4-addition,[1] whereas in the case of cyclopentadiene, 1,4- and *trans* addition is favored.[2] In acetylenic olefins such as vinylacetylene[3] and divinylacetylene[4] only addition to the double bond is observed.

On the other hand, it has been shown[5] that *t*-butyl hypochlorite is an efficient free-radical chlorinating agent and that allylic substitution rather than addition is the preferred reaction of *t*-butoxy radicals with many monoolefins. The reaction is effected in nonpolar solvents using light or free-radical sources as initiators.

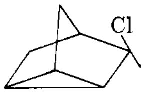
TABLE I

REACTION OF NORBORNENE WITH *t*-BUTYL HYPOCHLORITE (*t*-BuOCl)

	Starting materials					Reaction conditions			Product yields					
	Norbornene		*t*-BuOCl						1 + 2		3a		3b	
Run	g.	Mole	g.	Mole	Solvent, ml.	Temp., °C.	Time, hr.	Light[a]	g.	%[b]	g.	%[b]	g.	%[b]
1	94	1	43.2	0.4	None	26–30	1.5	Yes	9.9	19.2	32.4	40.0	7.3	9.0
2	72	0.82	17.7	0.16	CCl_4[c] (78)	0–5	3.8	Yes	4.4	21.0	21.9	66.3	4.2	13.0
3	94	1	21.6	0.2	C_6H_6 (133)	25–30	3.3	Yes	6.6	25.8	20.9	51.6	8.1	19.8
4	188	2	78	0.72	C_6H_6 (200)	<40	7	No	*d*		37.4	25.6	10.3	7.1
5	188	2	70	0.65	*t*-BuOH (90)	25–30	6.5	No	28.2	34.7	55.2	42.7	13.1	10.0
6	188	2	64	0.59	*t*-BuOH (200)	26	3	Yes	*d*	*d*	59.1	49.5	13.7	11.5
7	235	2.5	77	0.71	*t*-BuOH (200)	26	2.5	Yes	*d*	*d*	79.7	55.5	17.3	12.0

[a] Incandescent light, 400 w. [b] Based on *t*-BuOCl. [c] 26.1 g. of 2-*exo*-trichloromethyl-3-*endo*-chlorobicyclo[2.2.1]heptane formed by solvent participation. [d] Not determined.

The reaction of *t*-butylhypochlorite with norbornene under a variety of reactions conditions (see Table I) gives substitution products as well as addition products. Of the former, 3-nortricyclyl chloride (1) and 2-*exo*-chlorobicyclo[2.2.1]hept-5-ene (2) were identified as the two major constituents by comparison of their infrared spectra and their v.p.c. retention times with those obtained from authentic samples prepared by treating norbornadiene with hydrogen chloride in pentane.[6] The adducts were subsequently identified as 2-*exo*-*t*-butoxy-3-*endo*-chlorobicyclo[2.2.1]heptane (**3a**, formed in about 50% yield) and its *exo*-*cis* isomer (**3b**, ~10–15% yield), indicating that the initial attack of the *t*-butoxy radical proceeded from the less hindered *exo* side of the double bond. The isomers cannot be completely separated by fractional distillation. The optimum purity of **3a** by distillation techniques amounts to 90%; analytically pure **3a** can only be obtained by preparative vapor phase chromatography (v.p.c.). By the same technique **3b** was isolated in a purity of 91%.



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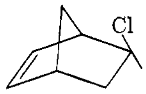

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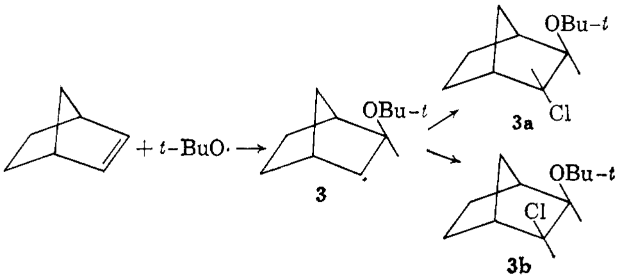

When the reaction of *t*-butyl hypochlorite with norbornene is carried out in CCl_4 as a solvent, the formation of the norbornene–CCl_4 adduct[7] is also observed. This is not surprising considering the fact that *t*-butyl hypochlorite is an excellent low-temperature radical generator.

Ether cleavage of **3a** with gaseous HCl at 100° affords the chlorohydrin **4** in 71% yield. In the n.m.r. spectrum of **4** (in CCl_4) the bridgehead protons are represented by broad unresolved signals at 2.13 and 2.40 p.p.m., the hydroxyl proton by a singlet at 3.37 p.p.m., and the protons geminal to the functional groups by signals at 3.55 and 3.82 p.p.m. Of the latter, the high-field signal is a sharp triplet while the low-

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(1) M. Anbar and D. Ginsberg, *Chem. Rev.*, **54**, 925 (1954).

(2) R. Riemschneider and R. Nehring, *Ann.*, **660**, 41 (1962).

(3) E. Tobler, D. E. Battin, and D. J. Foster, unpublished results.

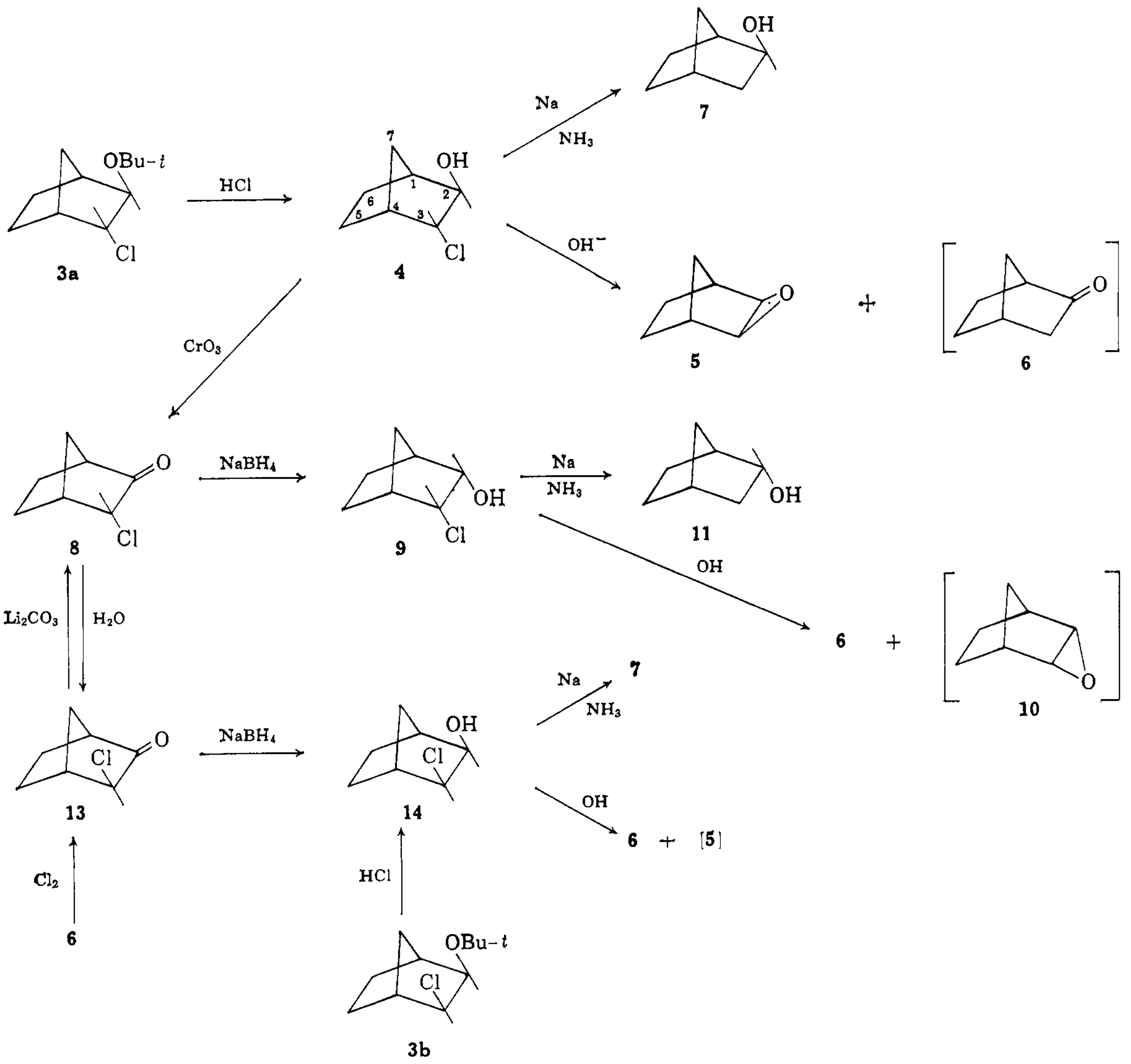
(4) A. L. Klebanskii, *et al.*, *J. Gen. Chem. USSR*, **16**, 1231 (1946).

(5) J. Kenner, *Nature*, **156**, 370 (1945); E. W. Belle and J. C. Cowan, *Ind. Eng. Chem.*, **41**, 849 (1949); H. M. Teeter, R. C. Beckman, C. Walling, and B. B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6108 (1960); C. Walling and W. Thaler, *ibid.*, **83**, 3877 (1961).

(6) L. Schmerling, J. P. Luvisi, and R. W. Welch, *ibid.*, **78**, 2820 (1956).

(7) E. Tobler and D. J. Foster, *J. Org. Chem.*, **29**, 2839 (1964).

CHART I



field signal is a broad, poorly resolved multiplet. The assignment of the two signals can be accomplished by comparing the spectrum with the one obtained from **3a**. Because the *t*-butyl group has a greater shielding effect than the hydrogen atom, substitution of the former for the hydroxyl proton should shift the resonance of its geminal proton upfield. The frequency of the 3.55-p.p.m. signal is in fact shifted to 3.26 p.p.m., whereas the frequency of the 3.82-p.p.m. signal is unaffected. The signal at 3.55 p.p.m. therefore represents H-2 and that at 3.82 p.p.m., H-3. Two couplings are observed in the 3.55-p.p.m. signal (the triplet is probably formed by the coincidence of two components of a four-line spectrum), both equal to 2.2 c.p.s. This fixes proton H-2 in the *endo* position, since an *exo* proton would exhibit a coupling close to 4.5 c.p.s.[8] The absence of a coupling greater than 2 is evidence that the proton H-3 is *trans* with respect to H-2. A *cis* relationship between H-2 and H-3 would be expected to show a coupling near 6 c.p.s.[8] The second coupling constant observed in the signal for H-2 may be due to interaction with the H-7-*anti* proton.[9]

Treatment of **4** with base yields as the main product the *exo* epoxide **5** and a trace of norcamphor (**6**) (see Chart I). This intramolecular displacement reaction strongly suggests that compound **4** has the *trans* configuration[10] with the hydroxyl group in *exo* position.

Reduction of **4** with sodium in liquid ammonia gives a 94.5% yield of *exo*-bicyclo[2.2.1]heptan-2-ol (**7**), thus definitely establishing the spacial configuration of the hydroxyl group in **4**.

Chromic acid oxidizes **4** to the chloro ketone **8** in an average yield of 50%. The n.m.r. spectrum of **8** shows three principal resonances: a doublet at 4.03 p.p.m., relative area 1, corresponding to the single hydrogen H-3; a broad band at higher field, relative area 2, corresponding to the bridgehead hydrogens H-1 and H-4; and a broad complex multiplet at highest field, relative area 6, corresponding to the methylene protons. The doublet character of the H-3 resonance (J_{12} = 4.5 c.p.s.) arises from spin–spin interaction of this proton with the bridgehead proton H-4.

Compound **8**, upon reduction with sodium borohydride, which is known to attack from the *exo* side giving

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[8] F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961).

[9] J. Meinwald, Y. C. Meinwald, and T. N. Baker, III, 18th National Organic Symposium of the American Chemical Society, Columbus, Ohio, June 16–20, 1963; *J. Am. Chem. Soc.*, **85**, 2514 (1963).

[10] P. D. Bartlett, *ibid.*, **57**, 224 (1935).

the more hindered alcohol in high proportions,[11] affords a new chlorohydrin **9** in 90% yield.

Base treatment of **9** results in the formation of **6** contaminated with a small amount of what is believed to be the *endo* epoxide[12,13] (**10**). This result strongly suggests that the two functional groups have a *cis* configuration.[10]

Reduction of **9** with sodium in liquid ammonia gives a 98% yield of *endo*-bicyclo[2.2.1]heptan-2-ol (**11**), confirming the *endo* position of the hydroxyl group in **9**.

The bromination of norcamphor has first been described by Woods and Roberts[14] and has been the subject of an extensive investigation by Krieger.[12] This bromination proceeds stereoselectively in high yield to 3-*exo*-bromobicyclo[2.2.1]heptan-2-one (**12**), suggesting another example of "*exo* addition" to the norbornene double bond.

The chlorination of norcamphor has been previously reported to give 3-chloronorcamphor.[15] However, the spacial configuration of the chlorine atom has not been elucidated.[16] When chlorination is carried out under conditions used for bromination, a 67% yield of 3-*exo*-chlorobicyclo[2.2.1]heptan-2-one (**13**) is obtained. The absence of absorption at 7.11 μ in the infrared[17] suggests that chlorination had occurred at the α-position, since such an absorption is characteristic of a CH_2 group adjacent to a carbonyl. A comparison of the n.m.r. data of the chloro ketone **13** with the one obtained from its isomer (**8**) confirms that the chlorine is in *exo* position, in analogy to the product obtained by the bromination of norcamphor. In the n.m.r. spectrum of **13**, the lowest field doublet occurs at 3.64 p.p.m. (J = 3.0 c.p.s.). A comparison of this value with that obtained from the isomeric chloro ketone **8** (4.03 p.p.m.) allows the assignment of the *endo*-chloro structure to **8** and the *exo*-chloro structure to **13**, for it is known that the chemical shift of the proton for the *exo*-substituted isomers (*endo* proton) is observed at higher field than for the corresponding proton (*exo*) in the *endo*-substituted isomer.[18] The reason **13** exhibits a coupling constant of 3.0 c.p.s. instead of zero was recently explained by Meinwald[9] who was able to demonstrate that *exo*-α-halo norcamphors show long-range spin–spin coupling between the *endo*-3 and *anti*-7 protons.

The chlorine atom in **13** is relatively unreactive towards hydrolysis even though it is α to a carbonyl group. Refluxing **13** with aqueous lithium carbonate results in partial isomerization to the *endo* isomer **8**. Practically the same behavior was observed by Krieger[12] for the analogous reaction of the corresponding bromoketone **12**.

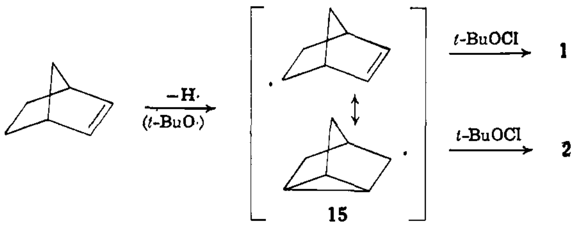
Reduction of **13** with sodium borohydride affords 3-*exo*-chloro-2-*exo*-hydroxybicyclo[2.2.1]heptane (**14**) in 87% yield, identical with the chlorohydrin obtained by ether cleavage of **3b**. Apparently the bulky chlorine atom renders the *exo* side of the molecule more hindered, so that the reagent attack is from the *endo* side resulting in the formation of an *exo* hydroxyl group. This result is in complete agreement with the findings of Krieger[12] who obtained the *exo*-*cis*-bromohydrin in 80% yield upon reduction of **12** with lithium aluminum hydride.

The n.m.r. spectrum of **14** shows quartets at 3.73 and 3.89 p.p.m., due to the protons H-2 and H-3. Two coupling constants are observed: 6.0 and 1.9 c.p.s. for H-2 and 6.0 and 1.6 c.p.s. for H-3. The large coupling constant signifies a *cis* configuration of vicinal protons and the small coupling constant indicates that the protons have an *endo* orientation. The small coupling is believed to be a long-range coupling between the 2- and 1-*endo* protons on the one hand and the 7-*anti* proton on the other.[9]

As a further proof of the *exo* position of the hydroxyl group, **14** was subjected to reduction with sodium in liquid ammonia to give a 95.5% yield of **7**. Base treatment of **14**, under similar conditions which were employed for the *endo*-*cis* isomer **9**, results in the formation of 37.7% **6** and 1.0% **5**, 54.6% **14** being recovered unchanged from the reaction mixture. This result is compatible with a *cis* configuration of the functional groups, since a *trans* arrangement would give the epoxide as the major product.[10] The slower reaction rate of **14** with base (as compared with the *endo*-*cis* isomer **9**) is probably due to steric hinderance towards attack by base.

The reaction of *t*-butyl hypochlorite with norbornene presented in this investigation appears to proceed according to a free-radical mechanism. Although some ionic participation cannot be entirely excluded, the nature of the reaction products and the fact that the reaction rate is considerably slowed down without the additional light source indicate a radical pathway.

The formation of the substitution products **1** and **2** can be satisfactorily explained in terms of a classical free-radical intermediate **15** and stabilized by resonance structures similar to those proposed for the reaction of norbornene with N-bromosuccinimide.[19]



Free-radical additions of various substrates to norbornenes have been reported to give *trans* addition,[7,20,21] *exo*-*cis* addition,[22,23] or a mixture of both.[24,25] A

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[11] J. Meinwald, J. K. Crandall, and P. G. Gassmann, *Tetrahedron*, **18**, 815 (1962), and references cited therein.

[12] H. Krieger, *Suomen Kemistilehti*, **31B**, 320 (1958).

[13] H. Kwart and T. Takeshita, *J. Org. Chem.*, **28**, 670 (1963).

[14] W. G. Woods and J. D. Roberts, *ibid.*, **22**, 1142 (1957).

[15] J. B. Miller, *ibid.*, **26**, 4905 (1961).

[16] In the meantime, J. Meinwald, Y. C. Meinwald, and T. N. Baker, III (see ref. 9), have demonstrated that the chlorination of norcamphor gives the 3-*exo*-chloro compound.

[17] S. A. Francis, *J. Chem. Phys.*, **19**, 942 (1951).

[18] T. J. Flautt and W. F. Erman, Abstracts of Papers, 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1961, p. 16Q.

[19] J. D. Roberts, E. R. Trumbull, Jr., W. Bennet, and R. Armstrong, *J. Am. Chem. Soc.*, **72**, 3116 (1950).

[20] S. J. Cristol and J. A. Reeder, *J. Org. Chem.*, **26**, 2182 (1961).

[21] D. I. Davies, *J. Chem. Soc.*, 3669 (1960).

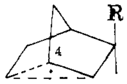
[22] S. J. Cristol and R. P. Arganbright, *J. Am. Chem. Soc.*, **79**, 6039 (1957).

[23] J. Weinstock, Abstracts, 128th National Meeting of the American Chemical Society, Minneapolis, Minn., Sept., 1955, p. 19O.

[24] N. A. LeBel, *J. Am. Chem. Soc.*, **82**, 623 (1960).

[25] J. A. Berson, *ibid.*, **76**, 4060, 5748 (1954); J. A. Berson and R. Swidler, *ibid.*, **75**, 4366 (1953).

bridged intermediate radical, similar in nature to the bromonium ion, was proposed to explain the stereospecific addition of hydrogen bromide.[26] However, the substantial number of nonspecific reactions throws doubt on the validity of such an intermediate. It is also possible to eliminate the possibility of formation of a nonclassical free radical **16**, which would be equivalent to the nonclassical carbonium ion. Such an intermediate radical would give rise to some 7-substitution due to chain transfer at C-4. The intermediate radical structure which is more or less generally accepted is the classical (open) structure, and the stereochemical results of addition reactions can be explained by the fact that the direction from which chain transfer occurs is controlled by steric factors. Thus, the exclusive *trans* addition in the case of polyhalomethanes[7] and *p*-toluenesulfonyl chloride[20] can be accounted for by the fact that the approach of the substrate molecule to the intermediate radical is inhibited from the *exo* side by steric interference of the large trichloromethyl and *p*-toluenesulfonyl group, respectively. Thus the chain transfer occurs from the *endo* side to give *trans* adducts. In the case of ethyl bromoacetate,[23] the steric blocking of the ethano bridge is greater than that of the carbethoxymethyl function with the result that both steps of the reaction occur from the less hindered or *exo* side of the molecule.



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The steric blocking of a *t*-butoxy group should be more effective than the ethano bridge, but not quite so effective as the bulky trichloromethyl or *p*-toluenesulfonyl group. The chain transfer step would therefore be expected to occur mainly, but not exclusively, from the *endo* side. The formation of *trans* and *cis* adducts in the ratio of about 4:1 confirm these considerations.

Experimental

All melting points are corrected. Infrared spectra (Beckman IR 4) were determined in carbon tetrachloride (2–7.5 μ) and carbon disulfide (7.5–15 μ) solution. N.m.r. spectra were determined with a Varian A60 spectrometer with tetramethylsilane as an internal standard. Vapor phase chromatography (Beckman GC-2A gas chromatograph) was performed on a 4-m. column containing 60:40 silicone 550–Carbowax 4000 on Chromosorb W (30–60) at 160 and 190° and a helium pressure of 55 p.s.i.

Reaction of Norbornene with *t*-Butyl Hypochlorite.—To a stirred mixture of 235 g. (2.5 moles) of norbornene and 200 ml. of *t*-butyl alcohol under a nitrogen atmosphere was added dropwise within 1.5 hr. 77 g. (0.71 mole) of *t*-butyl hypochlorite[27] at 26°. During this time the mixture was illuminated with a 100-w. incandescent light bulb. After one additional hour of stirring and illuminating, all the *t*-butyl hypochlorite had reacted and the reaction mixture was distilled. After removal of the low boilers at atmospheric pressure, the residue was distilled *in vacuo*. The data are summarized in Table II; the total yield of **3a** was 79.7 g. (55.5%). An analytical sample of **3a** from cut 4 was obtained by preparative v.p.c.: purity, 98.5%; $n^{20}\text{D}$ 1.4682; strong infrared absorption bands at 7.18, 7.32, 7.65, 8.13, 8.40, 8.95, 9.30, 9.67, 9.79, 10.53, and 12.30 μ.

Anal. Calcd. for $C_{11}H_{19}ClO$: C, 65.18; H, 9.45; Cl, 17.49. Found: C, 65.09; H, 9.22; Cl, 17.27.

Table II

Distn. cut	B.p., °C. (mm.)		Weight, g.	$n^{20}\text{D}$	Compd. according to v.p.c. (area%)		
					1+2	**3a**	**3b**
3	52–56	(0.4–1.1)	11.0	1.4716	12.9	73.4	9.5
4	53–55	(0.4)	15.0	1.4687	1.4	84.7	12.6
5	56–57	(0.45)	43.0	1.4685	0.1	81.5	17.3
6	57–58	(0.5)	26.0	1.4692	0.0	68.7	26.4

Compound **3b**, isolated in 91.1% purity from cut 6 by preparative v.p.c., had $n^{20}\text{D}$ 1.4742. Sharp infrared absorptions were at 7.16, 7.28, 7.97, 8.35, 8.71, 8.93, 9.13, 9.59, and 10.49 μ.

Anal. Calcd. for $C_{11}H_{19}ClO$: C, 65.18; H, 9.45; Cl, 17.49. Found: C, 64.29; H, 9.24; Cl, 16.72.

Ether Cleavage of 3a with HCl [2-*exo*-Hydroxy-3-*endo*-chlorobicyclo[2.2.1]heptane (4)].—A distillation cut (51.0 g.) containing 81.5% **3a** (41.6 g., 0.205 mole) was placed into a 250-ml. 3-neck flask provided with gas inlet tube, reflux condenser, and thermometer. The flask was heated with a steam bath and dry, gaseous HCl was bubbled through the liquid for 7 hr. Upon cooling, the purplish liquid solidified (37.1 g.). Hexane was added and the mixture was heated on the steam bath. After all the solids had dissolved, charcoal was added and the mixture was filtered in the heat. After cooling the filtrate, a white solid crystallized which was recrystallized twice from hexane to give 21.0 g. (70.7%) of **4**: m.p. 116–116.5°; infrared bands at 2.84, 2.95, 8.99, 9.43, 9.97, 10.58, 12.27, and 12.52 μ.

Anal. Calcd. for $C_7H_{11}ClO$: C, 57.34; H, 7.56; Cl, 24.18. Found: C, 57.10; H, 7.43; Cl, 24.23.

Phenylurethane had m.p. 118–119°.

Anal. Calcd. for $C_{14}H_{16}ClNO_2$: C, 63.28; H, 6.07; Cl, 13.34; N, 5.27. Found: C, 62.88; H, 5.94; Cl, 13.49; N, 5.53.

V.p.c. analysis of the combined mother liquors indicated the presence of 60.27% **4** and 28.5% **14**.

Reaction of 4 with Base.—A sample of 1.20 g. of **4** (8.2 mmoles) was refluxed with 3 g. of potassium hydroxide in 7 ml. of water for 2 hr. Extraction of the reaction mixture with ether gave 0.78 g. (86.5%) of a solid melting at 102–108°. Except for absorption bands at 5.71, 8.52, 9.38, 9.58, and 10.63 μ, the infrared spectrum of this product was identical with the one obtained from 2,3-*exo*-epoxybicyclo[2.2.1]heptane (**5**), prepared by oxidation of norbornene with peracetic acid. The additional absorption bands were due to the presence of norcamphor (**6**), as shown by comparison with the infrared spectrum from an authentic sample of **6** and by the melting point of its 2,4-dinitrophenylhydrazone (128.5–129.5°).

Anal. Calcd. for $C_{13}H_{14}N_4O_4$: C, 53.78; H, 4.86; N, 19.30. Found: C, 53.58; H, 5.12; N, 19.17.

Reduction of 4 with Sodium in Liquid Ammonia.—To 5.0 g. of **4** (0.034 mole) in a 250-ml. 4-neck flask provided with a stirrer, Dry Ice condenser, and gas inlet tube was added gaseous NH_3 (*ca.* 100 cc.) while the reaction flask was being cooled with a Dry Ice–acetone bath. Sodium (2 g., 0.085 g.-atom) was added to the stirred solution in four equal portions. After the addition of the last portion, the blue-purple color of the reaction mixture persisted. After 1 hr., the excess sodium was decomposed by addition of ammonium chloride and the liquid ammonia was allowed to evaporate. Water was then added to the residue; the solution was acidified with dilute sulfuric acid and extracted with ether. After drying over anhydrous magnesium sulfate, the ether was evaporated *in vacuo* to give 3.5 g. (94.5%) of a white solid, m.p. 113–117°. After two recrystallizations from pentane, the 2-*exo*-hydroxybicyclo[2.2.1]heptane (**7**) melted at 127–128° (lit.[28] m.p. 127–128°).

Anal. Calcd. for $C_7H_{12}O$: C, 74.93; H, 10.78. Found: C, 75.12; H, 10.61.

Phenylurethane had m.p. 141–142.5° (lit. m.p. 145–146°,[28] 140.6–141.4°[29]).

Anal. Calcd. for $C_{14}H_{17}NO_2$: C, 72.69; H, 7.41; N, 6.06. Found: C, 72.37; H, 7.61; N, 6.09.

Oxidation of 4 with Chromic Acid [3-*endo*-Chlorobicyclo[2.2.1]-heptan-2-one (8)].—To a cooled (ice bath) and stirred mixture of 49.2 g. of $K_2Cr_2O_7$ (0.164 mole), 750 ml. of water, 68 g. of concentrated sulfuric acid, and 300 ml. of acetic acid was added 10.0 g. (0.068 mole) of **4**. The mixture was stirred at 5° for 4.5 hr.

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(26) H. L. Goering, P. I. Abell, and B. F. Aycock, *J. Am. Chem. Soc.*, **74**, 3588 (1952).

(27) R. T. Arnold, *Org. Syn.*, **32**, 20 (1952).

(28) G. Komppa and S. Beckmann, *Ann.*, **512**, 172 (1934).

(29) J. D. Roberts, E. R. Trumbull, Jr., W. Bennett, and R. Armstrong, *J. Am. Chem. Soc.*, **72**, 3116 (1950).

after which time the ice bath was removed while stirring was continued overnight. A solution of 250 g. of sodium hydroxide in 250 ml. of water was then added dropwise to the reaction mixture with cooling. When the mixture was slightly alkaline, it was steam distilled, approximately 2 l. of distillate being collected. The distillate was saturated with sodium chloride and extracted with ether. After drying over anhydrous magnesium sulfate, the ether was evaporated *in vacuo*, leaving 5.2 g. (53%) of a viscous residue which solidified upon standing. Bulb distillation afforded a colorless, low-melting solid, distilling at a bath temperature of 80–100° at 3 mm. Vacuum sublimation yielded **8** as a waxy solid: m.p. 50–53°; principal infrared absorption bands at 5.60, 7.70, 8.19, 8.63, 9.30, 10.47, 10.63, 12.15, 12.42, and 13.23 μ.

Anal. Calcd. for C_7H_9ClO: C, 58.14; H, 6.27; Cl, 24.52. Found: C, 58.64; H, 6.56; Cl, 24.35.

Semicarbazone had m.p. 182–182.5° (187–188°).

Anal. Calcd. for $C_8H_{12}ClN_3O$: C, 47.66; H, 6.00; Cl, 17.59; N, 20.84. Found: C, 47.50; H, 6.39; Cl, 17.84; N, 20.39.

2,4-Dinitrophenylhydrazone had m.p. 154.5–155.5°; λ_{max} 232 mμ (ϵ 11,364), 250 (9990), 357 (20,068).

Anal. Calcd. for $C_{13}H_{13}ClN_4O_4$: C, 48.08; H, 4.04; Cl, 10.92; N, 17.25. Found: C, 48.31; H, 3.94; Cl, 10.72; N, 17.04.

Reduction of 8 with $NaBH_4$ [3-*endo*-Chloro-2-*endo*-hydroxybicyclo[2.2.1]heptane (9)].—To a stirred solution of 3.10 g. (21.4 mmoles) of **8** in 150 ml. of methanol was added dropwise at room temperature a solution of 3.5 g. of $NaBH_4$ in 35 ml. of water. At the end of the addition, the mixture was stirred for 3 hr. The mixture was then diluted with water, acidified with dilute sulfuric acid, and extracted with ether. The combined ether layers were washed with water and dried over calcium sulfate. Evaporation of the ether *in vacuo* gave 2.70 g. of crude **9** (86%), which after recrystallization from hexane and vacuum sublimation at 100° had m.p. 95–97°; principal infrared bands at 2.77, 7.62, 7.83, 8.80, 9.03, 9.35, and 13.29 μ.

Anal. Calcd. for $C_7H_{11}ClO$: C, 57.34; H, 7.56; Cl, 24.18. Found: C, 57.26; H, 7.74; Cl, 24.14.

Phenylurethane had m.p. 108.5–109.5°.

Anal. Calcd. for $C_{14}H_{16}ClNO_2$: C, 63.28; H, 6.07; Cl, 13.34; N, 5.27. Found: C, 63.04; H, 5.85; Cl, 13.43; N, 5.45.

Reduction of 9 with Sodium in Liquid Ammonia.—A sample of **9** (0.80 g., 5.47 mmoles) was reduced with sodium in liquid ammonia as described for **4** to give 0.60 g. (98%) of crude 2-*endo*-hydroxybicyclo[2.2.1]heptane (**11**), which after two recrystallizations from pentane melted at 149–150.5° (lit.[28] m.p. 149–150°).

Anal. Calcd. for $C_7H_{12}O$: C, 74.93; H, 10.78. Found: C, 75.32; H, 10.49.

Phenylurethane had m.p. 157.5–159° (lit. m.p. 159–160°,[28] 157.4–158.2°[29]).

Anal. Calcd. for $C_{14}H_{17}NO_2$: C, 72.69; H, 7.41; N, 6.06. Found: C, 72.46; H, 7.09; N, 5.99.

Reaction of 9 with Base.—Refluxing 0.40 g. of **9** (2.73 mmoles) with a solution of 0.20 g. of sodium hydroxide in 5 ml. of water and 5 ml. of ethanol for 2 hr. gave 0.22 g. (73.4%) of a white solid melting at 72–81°. The infrared spectrum indicated that this material was mainly **6**, contaminated with some epoxybicyclo[2.2.1]heptane (**10**). According to v.p.c., the mixture consisted of 89.7% **6** and 10.3% **10**.

Practically the same result was obtained, when **9** together with an excess of dry, powdered $Ca(OH)_2$ was heated in a sealed tube to 200° for 3–4 hr.

Chlorination of Norcamphor (6) [3-*exo*-Chlorobicyclo[2.2.1]heptan-2-one (13)].—A 50-g. sample of **6** (0.45 mole) was placed into a 125-ml. flask provided with a magnetic stirrer, reflux condenser, thermometer, and a gas inlet tube. The flask was placed on a hot steam bath and chlorine gas was bubbled through the melted **6**. After 15.5 g. of chlorine had been taken up (calculated, 16.15 g.; *ca.* 2.5 hr.), the chlorination was interrupted and the product was distilled. The material (**13**) boiled at 82–83° (3 mm.) and had $n^{20}D$ 1.4985; principal infrared bands at 5.60, 6.82, 7.63, 8.51, 8.98, 9.30, 10.63, 11.83, 13.33, and 14.38 μ.

Anal. Calcd. for C_7H_9ClO: C, 58.14; H, 6.27; Cl, 24.52. Found: C, 57.99; H, 6.31; Cl, 24.25.

According to v.p.c., the yield was 44.4 g. (67.3%). The isomeric chloro ketone **8** was formed in 2.6% yield.

2,4-Dinitrophenylhydrazone of **13** had m.p. 157.5–158.5°. Mixture melting point with the 2,4-dinitrophenylhydrazone of **8**, 129.5–136.0°; λ_{max} 229 mμ (ϵ 9335), 250 (7690), 354 (20,943).

Anal. Calcd. for $C_{13}H_{13}ClN_4O_4$: C, 48.08; H, 4.04; Cl, 10.92; N, 17.25. Found: C, 47.97; H, 4.11; Cl, 10.42; N, 16.99.

Reaction of 13 with Aqueous Lithium Carbonate.—A mixture of 2.0 g. of **13** (13.6 mmoles), 5.0 g. of Li_2CO_3, and 100 ml. of water was refluxed for 23 hr. Ether extraction of the reaction mixture afforded 1.2 g. of a yellow oil. The infrared spectrum of the product indicated a mixture of **8** and **13**. According to v.p.c., the mixture consisted of 5% **6**, 35.5% **13**, and 54% **8**.

3-*exo*-Chloro-2-*exo*-hydroxybicyclo[2.2.1]heptane (14). A. Reduction of 13 with $NaBH_4$.—Reduction of 5.20 g. of **13** (36 mmoles) in 500 ml. of methanol with 5.5 g. of $NaBH_4$ in 50 ml. of water as described for the reduction of **8** gave 4.60 g. (87%) of crude **14**. Bulb distillation at a bath temperature of 80–90° and a pressure of 3 mm. afforded **14** as a water-clear liquid, $n^{20}D$ 1.5110, f.p. 16–18°.

Anal. Calcd. for $C_7H_{11}ClO$: C, 57.34; H, 7.56; Cl, 24.18. Found: C, 57.16; H, 7.45; Cl, 24.48.

Phenylurethane had m.p. 149.5–150.5°.

Anal. Calcd. for $C_{14}H_{16}ClNO_2$: C, 63.28; H, 6.07; Cl, 13.34; N, 5.27. Found: C, 63.69; H, 6.07; Cl, 13.12; N, 5.27.

B. **Ether Cleavage of 3b.**—A fraction (37.5 g.) containing 63.5% **3a** and 20.5% **3b** was treated with HCl as described for the ether cleavage of **3a** to give 24.5 g. of a product consisting of 74% **4** and 21.8% **14**. The isolation of **14** by preparative-scale v.p.c. afforded **14** in 90% purity ($n^{22}D$ 1.5088). The infrared spectrum was identical with **14** obtained from A; phenylurethane had m.p. 148.5–150°; mixture melting point with phenylurethane from A was 149–150°.

Reduction of 14 with Sodium in Liquid Ammonia.—Reduction of 2.90 g. of **14** (19.8 mmoles) with sodium in liquid ammonia as described for **4** gave 2.10 g. (95.5%) of **7**; phenylurethane had m.p. 141–142.5°; mixture melting point with the phenylurethane of **7** obtained by reducing **4** was 141–142.5°.

Reaction of 14 with Base.—Refluxing 0.70 g. of **14** (4.78 moles) with a solution of 0.48 g. of sodium hydroxide in 7.5 ml. of water and 7.5 ml. of ethanol for 3.5 hr. gave 0.49 g. of an oil, which according to v.p.c. consisted of 1.0% **5**, 37.7% **6**, and 54.6% unchanged **14**.

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