several recrystallizations from petroleum ether brought the melting point to 42.5–43.5° (uncor.).

Anal. Calcd. for $C_8H_{11}ClO$: C, 60.5; H, 7.0; Cl, 22.4. Found: C, 60.1; H, 6.9; Cl, 22.1.

The *p*-**nitrobenzoyl ester** was prepared and recrystallized from methanol–water, m.p. 104.0–105.5° (cor.).

Anal. Calcd. for $C_{15}H_{14}ClNO_4$: C, 58.5; H, 4.6; Cl, 11.5; N, 4.6. Found: C, 58.4; H, 4.4; Cl, 11.5; N, 4.6.

3-Chloro-4-oxobicyclo[3.2.1]oct-2-ene (VII).—A mixture of 2.31 g. (0.0146 mole) of 3-chloro-4-*exo*-hydroxybicyclo[3.2.1]-oct-2-ene (VI) and 25 g. of manganese dioxide[27] in 200 ml. of pentane and 50 ml. of anhydrous ether was stirred at room temperature for 5.5 hr. The manganese dioxide was removed by filtration through Celite on sintered glass, the filtrate was dried over magnesium sulfate, and the solvent removed. The product (1.36 g., 60% of theoretical, $n^{25}\mathrm{D}$ 1.5283) showed 10% impurity by n.m.r. analysis.

Anal. Calcd. for C_8H_9ClO: Cl, 22.6. Found: Cl, 22.2.

3-Chloro-*endo*-4-hydroxybicyclo[3.2.1]oct-2-ene (VIII).—A solution of 1.17 g. (0.0075 mole) of 3-chloro-4-oxobicyclo[3.2.1]-oct-2-ene (VII) in 15 ml. of ether was added slowly to a suspension of 0.57 g. (0.0150 mole) of lithium aluminum hydride in 25 ml. of ether. The mixture was stirred for 30 min. at room temperature, decomposed with water, and filtered through Celite. The filtrate was dried over magnesium sulfate and the solvent removed. The residue solidified on chilling (0.94 g., 80%). As determined by n.m.r. it had a purity of 90%, the contaminant being the *exo* isomer. They could not be separated by vapor phase chromatography.

The *p*-nitrobenzoate was prepared and recrystallized from ethanol–water, m.p. 88–90° (uncor.).

Anal. Calcd. for $C_{15}H_{14}ClNO_4$: C, 58.5; H, 4.6. Found: C, 58.2; H, 4.7.

Treatment of Norbornadiene (IX) with Dichlorocarbene.—Several treatments of IX with dichlorocarbene generated by the action of potassium *t*-butoxide on chloroform, as in the preceding example, gave 8–21% yields, on a weight basis, of crude product containing as many as six components determined by vapor phase chromatography. The major component of this mixture could not be obtained in better than 90% purity by various low-temperature distillations, b.p. 45° (0.55 mm.), 30° (0.4 mm.). The n.m.r. spectral data (Table I) clearly indicate that this substance is 3,3-dichloro-*exo*-tricyclo[$3.2.1.0^{2,4}$]oct-6-ene (X). Furthermore, upon standing, the n.m.r. and infrared spectra changed completely to those of the rearrangement product, *exo*-3,4-dichlorobicyclo[3.2.1]octa-2,6-diene (XI).

***exo*-3,4-Dichlorobicyclo[3.2.1]octa-2,6-diene (XI).**—A crude reaction product as obtained in the preceding example, when submitted to slow distillation through a 20-cm. concentric-tube fractionation column, gave pure XI, 55% by weight, b.p. 83° (4.4 mm.), $n^{25}\mathrm{D}$ 1.5400, d^{20}_{4} 1.272.

Anal. Calcd. for $C_8H_8Cl_2$: C, 54.9; H, 4.6; mol. wt., 175. Found: C, 55.2; H, 4.6; mol. wt., 175.

3-Chlorobicyclo[3.2.1]octa-2,6-diene (XII).—In an inert atmosphere, 12.47 g. (0.069 mole) of *exo*-3,4-dichlorobicyclo[3.2.1]-octa-2,6-diene (XI) of 78% purity (containing 11% each of two unidentified components as estimated by vapor phase chromatography) in 50 ml. of anhydrous ether was added rapidly to a refluxing suspension of 3.1 g. (0.082 mole) of lithium aluminum hydride in 300 ml. of ether. The mixture was stirred and heated at reflux for 5 hr., cooled, treated with 100 ml. of 5% aqueous potassium hydroxide, filtered through Celite, and extracted with ether. The extract was dried over magnesium sulfate and distilled at reduced pressure through a 10-cm. Vigreux column, yielding several fractions: (a) b.p. 60° (19 mm.), 2.00 g.; (b) b.p. 108–111° (19 mm.), 7.25 g.; and (c) residue, 0.79 g.

Fraction b was composed of 73% of the starting material and 10% and 17% of the original unknowns, as estimated by vapor phase chromatography.

Fraction a was 95% pure XII by vapor phase chromatography, representing 53.5% of the theoretical yield and 31% conversion. Redistillation gave pure XII, b.p. 75–76° (31 mm.), $n^{25}\mathrm{D}$ 1.5143, d^{20}_{4} 1.117.

Anal. Calcd. for C_8H_9Cl: C, 68.4; H, 6.5; Cl, 25.2. Found: C, 68.0; H, 6.6; Cl, 25.0.

A second similar run gave a 98% yield and 55% conversion.

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(27) O. Mancera, G. Rosenkrantz, and F. Sondheimer, *J. Chem. Soc.*, 2190 (1953).

Reactions Related to the Addition of Dichlorocarbene to Norbornylene

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Addition of dichlorocarbene to norbornylene at 0° gave a $C_8H_{10}Cl_2$ product isomeric with the expected dichlorocyclopropane derivative. The isomer was shown to be 3,4-dichlorobicyclo[3.2.1]octene-2. Similarly, cyclopentene gave a 40% yield of a 1:1 mixture of the normal product, 6,6-dichlorobicyclo[3.1.0]hexane, and its isomer, 2,3-dichlorocyclohexene. The latter was shown to arise from the former during work-up. Addition of dichlorocarbene to cyclohexene and cycloheptene gave only normal (dichlorocyclopropane) products. The order of stability of the adducts described is consistent with strain being the controlling factor. A stable purple carbonium ion was formed by treatment of either dichlorocarbene adduct of cyclopentene with strong Lewis acids.

In the course of investigating the chemistry of the addition of halocarbenes to various unsaturates, a ring expansion reaction was observed in which 6,6-dichlorobicyclo[3.1.0]hexane rearranged to 2,3-dichlorocyclohexene. In order to determine how general this reaction might be, other dichlorocarbene adducts of alicyclic olefins and some acyclic olefins were examined.

The rearrangement of cyclopropyl to allylic derivatives is a known reaction. For example, Roberts and Chambers[1] obtained allyl acetate from the solvolysis of cyclopropyl tosylate in acetic acid at 175°. Similarly, Lipp and Buchkremer[2] obtained only allyl alcohol from the diazotization of cyclopropylamine. The corresponding rearrangement of dichlorocyclopropyl derivatives, obtained by dichlorocarbene addition to cyclic olefins, is unique in that the product is ring expanded.

Examples of such ring expansions have been observed by other workers.[3] In 1881 Giamician and Dennsted[3a] reported that the reaction of the potassium salt of pyrrole with chloroform gave 3-chloropyridine. Parham and Reiff[3b] obtained β-chloronaphthalene from the addition of dichlorocarbene to indene and, later,[3c]

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(1) J. D. Roberts and V. C. Chambers, *J. Am. Chem. Soc.*, **73**, 5034 (1951).

(2) P. Lipp and J. Buchkremer, *Ann.*, **499**, 1 (1932).

isolated the intermediate adduct, 1,1-dichloro-1a,6a-dihydrocycloprop[*a*]indene. The latter compound rearranged at 50° in ethanol, in a first-order reaction, to give β-chloronaphthalene and hydrogen chloride. Skell, *et al.*,[3d,e,f] reported that silver ion rearrangement of 6,6-dihalobicyclo[3.1.0]hexane gave the 2-bromo-2-cyclohexen-1-ol ring system and indicated that the 5–3 ring was 200 times as reactive as the corresponding 6–3 ring system. Other examples of halocarbene–olefin adducts ring expanding have since been reported. Cyclopentadiene and dichlorocarbene gave chlorobenzene.[3g] Monochlorocarbene[3h] gave pyridine from pyrrole and quinoline from indole.

In several cases, the intermediate dichlorocarbene adduct was isolated and then rearranged (with the loss of hydrogen chloride). The adduct of Δ^2-dihydropyran, on boiling with quinoline, gave 3-chloro-6,7-dihydrooxepine.[3i] The dichlorocarbene adducts of butadiene and cyclohexene, on pyrolysis at 500°, gave 3-chlorocyclopentadiene[3j] and cycloheptatriene,[3k] respectively. The latter two reactions are probably radical in nature, while those cited previously appear to be ionic processes.

Recently, Winstein and Sonnenberg[3l] reported the facile rearrangement of 6,6-dibromobicyclo[3.1.0]hexane to 2,3-dibromocyclohexene.

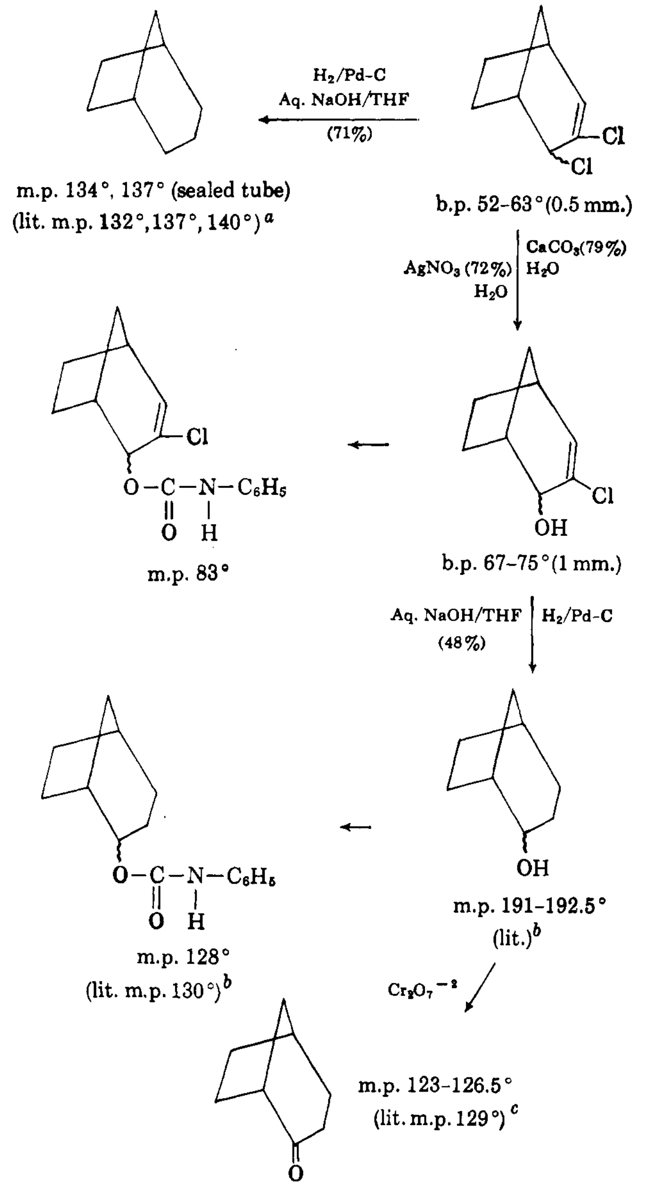
The purpose of the present paper is to present additional examples of dihalocyclopropane ring expansions and to evaluate the effect of structure on the ease of such reactions.

Results

Addition of Dichlorocarbene to Norbornylene.—This reaction gave a 15% yield of a material with good analysis for a $C_8H_{10}Cl_2$ compound, but whose physical and chemical properties indicated it to be an olefin. It had a 6.1-μ band in the infrared and showed a single vinyl hydrogen split by a bridgehead hydrogen (n.m.r.). It also had a single hydrogen chemically shifted by a chlorine atom attached to the same carbon and further split by a bridgehead hydrogen. One chlorine atom was reactive to both SN2 and SN1 reactions (allylic), while the second was inert (vinylic). Hydrogenation gave the known bicyclo[3.2.1]octane. Hydrogenation of the chloroallyl alcohol, obtained by hydrolysis of the allylic chlorine, gave the known bicyclo[3.2.1]-octanol-2. Table I summarizes the proof of structure which shows this isomer to be 3,4-dichlorobicyclo-[3.2.1]octene-2.

Table I

Proof of Structure of 3,4-Dichlorobicyclo[3.2.1]octene-2



[a] Very volatile; m.p. sensitive to impurities. W. Von E. Doering and M. Farber [*J. Am. Chem. Soc.*, **71**, 1514 (1949)] report m.p. 141° (sealed tube); J. W. Barrett, R. P. Linstead [*J. Chem. Soc.*, 613 (1936)] report m.p. 132°; M. S. Newman and Y. T. Yu [*J. Am. Chem. Soc.*, **74**, 507 (1952)] report m.p. 136.8–137.2° (sealed tube). [b] For mixture of *exo–endo*, 184–190° melting point; Prof. H. M. Walborsky, private communication and *ibid.*, **81**, 4709 (1959); Doering, *et al.*, *ibid.*, **71**, 1514 (1949), report m.p. 183–184° for the bicyclo[3.2.1]-octanol-2 of unspecified stereochemistry. The phenylurethan had a melting point of 130°. [c] K. Alder and E. Windemuth, *Ber.*, **71**, 2404 (1938), report m.p. 129°. We prepared an impure DNP, m.p. 135°; the melting point of this derivative reported in footnote *b* was 137.5–139°.

Other $C_8H_{10}Cl_2$ isomers were ruled out on the basis of reactivity or physical properties of their derivatives (*e.g.*, dichlorobicyclo[2.2.2]octenes, dichlorobicyclo-[5.1.0]octenes, dichlorobicyclo[4.2.0]octenes, dichlorobicyclo[3.3.0]octenes, and dichlorospiro[5.2]octenes). The properties of bicyclo[4.1.1]octane or any of its derivative corresponding to those in Table IV were not found in the literature. It is unlikely, however, that the physical properties of these derivatives would all correspond so closely to those of the bicyclo[3.2.1]-octane system. Further, no dichlorobicyclo[4.1.1]-octene could both fit the observed n.m.r. data and the high SN1 and SN2 activity of one of the chlorine atoms. Finally, such a deep seated rearrangement is required to get to this ring system that, taken with the previous evidence, it is excluded as a possibility.

Likewise, dichlorobicyclo[3.2.1]octenes other than the 3,4-dichloro derivative can be eliminated on the basis of the high SN2 reactivity of the parent dihalide.

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(3) (a) G. L. Giamician and M. Dennstedt, *Ber.*, **14**, 1153 (1881); (b) W. E. Parham and H. E. Reiff, *J. Am. Chem. Soc.*, **77**, 1177 (1955); (c) W. E. Parham, H. E. Reiff, and P. Schwartzentruber, *ibid.*, **78**, 1437 (1956); (d) P. S. Skell and S. R. Sandler, *ibid.*, **80**, 2024 (1958); (e) S. R. Sandler, *Dissertation Abstr.*, **21**, 61 (1960); (f) P. S. Skell, R. E. Glick, S. R. Sandler, and L. Gatlin, Fourth Report of the Petroleum Research Fund, 1959, p. 82; (g) A. P. ter Borg and A. F. Bickel, *Rec. trav. chim.*, **80**, 1217 (1961); (h) G. L. Closs and G. M. Schwartz, *J. Org. Chem.*, **26**, 2609 (1961); (i) W. E. Parham and E. E. Schweizer, *J. Am. Chem. Soc.*, **82**, 4085 (1960); (j) N. P. Neureiter, *J. Org. Chem.*, **24**, 2044 (1959); (k) H. E. Wynberg, *ibid.*, **24**, 264 (1959); (l) S. J. Winstein and J. Sonnenberg, *ibid.*, **27**, 748 (1962).

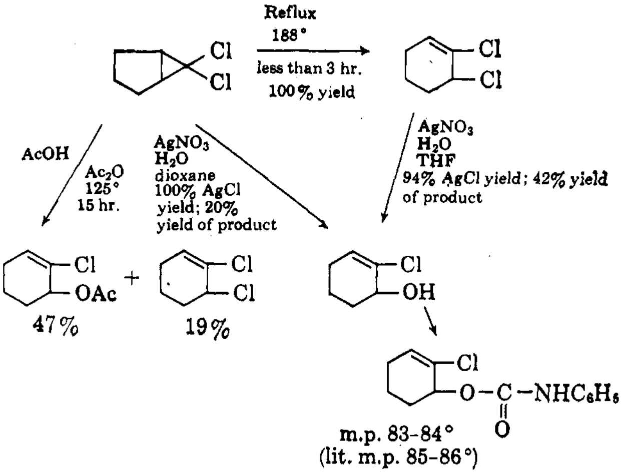
Addition of dichlorocarbene and dibromocarbene to norbornadiene gave the related rearranged products 2,3-dihalobicyclo[3.2.1]octadiene-2,6 in up to 25% yield.[4]

Addition of Dichlorocarbene to Cyclopentene.—In contrast to the addition of dichlorocarbene and dibromocarbene to bicyclo[2.2.1] olefins, where rearrangement of the dichlorocyclopropane proceeds with exceptional ease and the intermediate has not yet been isolated, addition of dichlorocarbene to cyclopentene gave 6,6-dichlorobicyclo[3.1.0]hexane. A higher boiling isomer also was obtained. This was shown to be 2,3-dichlorocyclohexene, formed by rearrangement during the distillation of the product. Table II summarizes the reactions of the isomeric $C_6H_8Cl_2$ compounds.

Isolation of the known alcohol, phenylurethan, and acetate of 2-chloro-3-hydroxycyclohexene[5] as outlined in Table II along with its physical properties,[5] indicates that the isomeric $C_6H_8Cl_2$ olefin is 2,3-dichlorocyclohexene.

TABLE II

REACTIONS OF ISOMERIC $C_6H_8Cl_2$ COMPOUNDS



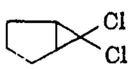
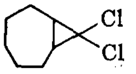
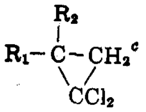
Solvolysis of either $C_6H_{10}Cl_2$ isomer in 90% formic acid gave copious amounts of hydrogen chloride gas and left dark polymeric products, presumably derived from 2-chlorocyclohexadiene-1,3. These observations parallel those reported earlier[3d,e,f] by Skell, *et al.*, for the dibromocarbene, dichlorocarbene, and chlorobromocarbene adducts of cyclopentene.

Addition of Dichlorocarbene to Cyclohexene and Cycloheptene.—Addition of dichlorocarbene to the subject olefins gave only the dichlorocyclopropane adducts in 59% and 43% isolated yields. The adducts were very stable and could be refluxed under nitrogen without any sign of isomerization.[6]

TABLE III

RELATIVE EASE OF REARRANGEMENT OF DICHLOROBICYCLO[x.1.0] SYSTEMS

(x = 3, 4, and 5)

	Heat	Reagent 0.1 N $AgNO_3$ in ethanol	$AlCl_3$[a]	Other
	100% in <3 hr. at 153–188°; No reaction in 2 hr. at 75° in tetrahydrofuran	100% in several hours at 25°	Intense purple color,[b] stable but discharged by water 7% isomerization in 5 hr. at 25°	BCl_3, $AgBF_4$, BF_3 all gave stable purple to red colors
	Stable for 8 hr. at 196–199°	No reaction in several weeks at 25°	No reaction at 25° (6 hr.)	...
	Stable for 5 hr. at 221–225°	No reaction in several weeks at 25°	No reaction at 25° (6 hr.)	...
[c]	...	No reaction in several weeks at 25°	No reaction at 25° (6 hr.) for compound with $R_1 = C_6H_5$; $R_2 = H$	...

[a] 5–10% by weight of dry $AlCl_3$ in liquid compound at 25°. [b] 2,3-Dichlororocyclohexene gave a similar intense purple color. [c] R_1 and R_2 were various combinations of C_6H_5, CH_3, H, CH=CH$_2$, and Cl (see Table IV). For $R_1 = R_2 = C_6H_5$ a silver mirror formed in a few days.

Table III sumarizes the ring opening tendencies of 6,6-dichlorobicyclo[3.1.0]hexane, 7,7-dichlorobicyclo[4.1.0]heptane, and 8,8-dichlorobicyclo[5.1.0]octane. It should be noted that in no case did any dichlorocyclopropane derivative (Table IV) react with silver nitrate in an S$_N$1 reaction despite the fact that stable carbonium ions would be produced.

The intense, stable purple colors observed when either 6,6-dichlorobicyclo[3.1.0]hexane or its isomer, 2,3-dichlorocyclohexene, is treated with strong Lewis acids presumably arise from condensation reactions which give carbonium ions in conjugation with a long polyunsaturated system. Such stable cations have been described recently by DeVries.[7]

A summary of the compounds prepared along with their physical properties and analyses is given in Table IV.

Discussion

The relative ease of rearrangement of the dichlorocarbene and dibromocarbene adducts of norbornylene, norbornadiene, and cyclopentene, in sharp contrast to

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(4) G. Fuller and L. Glover, Shell Development Co., unpublished results; also J. A. Yankeelov, *Thesis Abstr.*, **20**, 3085 (1960).

(5) M. Mousseron and R. Jacquier, *Bull. soc. chim. France*, **1950**, 648 (1950).

(6) H. E. Winberg, *J. Org. Chem.*, **24**, 264 (1959), reported that 7,7-dichlorobicyclo[4.1.0]heptane cracks to give 20% cycloheptatriene and 37% toluene at 500°.

(7) L. DeVries, *J. Am. Chem. Soc.*, **83**, 2392 (1961).

TABLE IV

PHYSICAL PROPERTIES AND ANALYSIS OF COMPOUNDS PREPARED

					Analyses, %							
					Calcd.				Found			
Compound	Yield, %	B.p., °C. (mm.)	n^{20}_D	Molecular formula	C	H	Cl	Other	C	H	Cl	Other
1-Vinyl-2,2-dichlorocyclopropane	63	125	1.4720^{25}	$C_5H_6Cl_2$	44.1	4.4	51.5		43.7	4.5	50.7	
1,1-Dimethyl-2,2-dichlorocyclopropane	39	120.5–121.0[c]	1.4472^{25}[c]	$C_5H_8Cl_2$								
1-Phenyl-2,2-dichlorocyclopropane	47	95–96 (6)	1.5523	$C_9H_8Cl_2$	57.8	4.3	37.9		57.9	4.3	37.5	
1,1-Diphenyl-2,2-dichlorocyclopropane	51	112–113, m.p.	...	$C_{15}H_{12}Cl_2$	68.5	4.6	26.9		68.5	4.6	26.8	
1,1-Dichlorobicyclo[4.1.0]heptane	59	81 (15)[d]	1.5022[d]	$C_7H_{10}Cl_2$	50.9	6.1	43.0		50.9	6.2	42.5	
1,1-Dichlorobicyclo[3.1.0]hexane	40[a]	69 (20)	1.4985	$C_6H_8Cl_2$	47.7	5.3	47.0		47.8	5.4	46.4	
8,8-Dichlorobicyclo[5.1.0]octane	43	50–53 (1)	1.5028	$C_8H_{12}Cl_2$	53.6	6.8	39.6	...	53.6	6.7	40.3	...
2,2,2′,2′-Tetrachlorobicyclopropyl	0.5[b]	77.1–78.0, m.p.	...	$C_6H_6Cl_4$	32.8	2.7	64.5	...	32.9	2.8	64.8	...
1-Methyl-1-vinyl-2,2-dichlorocyclopropane (plus 5% of 1-isopropenyl-2,2-dichlorocyclopropane	70	81–83 (110)	1.4785	$C_6H_6Cl_2$	47.8	5.4	46.8	...	48.2	5.4	46.5	...
1-Vinyl-1,2,2-trichlorocyclopropane (plus 20% of 1-(α-chlorovinyl)-2,2-dichlorocyclopropane	37	71.0–71.5 (36)	1.4998	$C_5H_5Cl_3$	35.0	2.9	62.1	...	35.2	3.0	61.6	...
3,4-Dichlorobicyclo[3.2.1]octene-2	15	52–63 (0.5–0.8)	1.5262–1.5357	$C_8H_{10}Cl_2$	54.3	5.7	40.0	...	54.6	5.7	39.7	...
3-Chloro-4-hydroxybicyclo[3.2.1]-octene-2	79	67–75 (1)	1.5333	$C_8H_{11}ClO$	60.5	6.9	22.4	0.63 equiv./100 g. hydroxyl No. sap. Cl	60.1	7.0	22.4	0.57 equiv./100 g. hydroxyl 0.068 equiv./100 g. sap. Cl
Phenylurethan of 3-chloro-4-hydroxybicyclo[3.2.1]octene	50	82.0–82.8, m.p.	...	$C_{15}H_{16}ClNO_2$	65.0	5.8	12.8	5.06 N	65.1	5.8	12.8	5.08 N
2-Hydroxybicyclo[3.2.1]octane	48; 99% H_2 uptake[e]	191–192.5, m.p. (sealed tube)	...	$C_8H_{14}O$	76.1	11.2	...	...	76.1	11.2	...	...
Phenylurethan of 2-hydroxybicyclo-[3.2.1]octane	50	127.5–128.0, m.p.	...	$C_{15}H_{19}NO_2$	73.4	7.8	...	5.71 N	73.0	7.8	...	5.69 N
Bicyclo[3.2.1]octane	71; 99 H_2 uptake; 97 HCl	136.5–138.0, 133.2–134.0 (sealed tube)[e]	...	C_8H_{14}	87.2	12.8	...	...	86.9	12.8	0.3	...
2,3-Dichlorocyclohexene	100	90 (20)[f]	1.5159	$C_6H_8Cl_2$	47.7	5.3	47.0	...	47.8	5.4	46.5	...
2-Chloro-3-acetoxycyclohexene	47	106 (15)[g]	1.4804^{25}	$C_8H_{11}ClO_2$	55.0	6.3	20.4	0.57 equiv./100 g. ester	54.8	6.3	20.6 (0.9 sap Cl)	0.58 equiv./100 g. ester
2-Chloro-3-hydroxycyclohexene	20; 42	86–87 (15)[h]	1.5088^{25}	C_6H_9ClO	54.4	6.8	26.8	0.75 equiv./100 g. hydroxyl	51.9	6.5	25.5	0.76 equiv./100. g hydroxyl
Phenylurethan of 2-chloro-3-hydroxycyclohexene	...	83–84,[i] m.p.	...	$C_{13}H_{14}NO_2Cl$	62.1	5.6	14.1	5.56 N	62.3	5.8	13.8	5.53 N

[a] About half was converted to 2,3-dichlorocyclohexene on distillation. [b] Isolated from reaction of dichlorocarbene with butadiene. [c] Lit.[10] b.p. 118–120°; n^{20}_D 1.4461. [d] Lit.[10] b.p. 78–79° (15 mm.); n^{23}_D 1.5014. [e] Volatile solid purified by sublimation; sensitive to impurities. [f] Properties reported for mixture of 2,3- and 1,2-dichlorocyclohexene: b.p. 85–87° (17 mm.); n^{20}_D 1.5061, ref. 5. [g] Lit.[5] b.p. 107–108° (15 mm.); n^{25}_D 1.4805. [h] Lit.[5] b.p. 86–87° (15 mm.); n^{25}_D 1.5066. [i] Lit.[5] m.p. 85–86°.

the relative stability of the corresponding adducts of cyclohexene and cycloheptene, is no doubt due to the added strain in the former systems. Even in cases where dichlorocyclopropanes (Table III) would give stable carbonium ions, no sign of rearrangement was noted with silver nitrate. For example, the dichlorocyclopropanes derived from styrene, *asym*-diphenylethylene, isobutylene, butadiene, isoprene, and chloroprene were all relatively stable to this reagent at room temperature despite the fact that ring opening of these compounds would lead to stable benzylic, tertiary or allylic carbonium ions. The stability of the intermediate carbonium ion does not appear to be important. The dichlorocarbene adducts of cyclopentene, cyclohexene, and cycloheptene give cyclohexenyl, cycloheptenyl, and cyclooctenyl carbonium ions on ring expansion. In saturated cyclic systems the seven- and eight-membered carbonium ions form much faster than the six-membered analog. It is probable that the same relation would hold for the unsaturated analogs just described.[8]

Experimental[9]

Preparation of Dichlorocarbene Adducts.—The dichlorocarbene adducts generally were prepared at 0–25° using excess olefin and chloroform as solvent. Somewhat better yields were obtained by adding the potassium *t*-butoxide to a solution of the olefin in chloroform rather than chloroform to the alkoxide suspended in the olefin. The procedures were similar to those described earlier.[10] The preparation of 3,4-dichlorobicyclo[3.2.1]octene-2, 8,8-dichlorobicyclo[4.1.0]octane, and 6,6-dichlorobicyclo-[3.1.0]-hexane are given as examples.

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[8] For example, see the discussion on stability of carbonium ion *vs.* ring size in A. Streitwieser's review [*Chem. Rev.*, **56**, 571 (1956)].

[9] Melting and boiling points are uncorrected; δ values are in p.p.m from tetramethylsilane.

[10] W. Von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **76**, 6162 (1954); P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956).

3,4-Dichlorobicyclo[3.2.1]octene-2.—To a stirred solution of norbornylene (294 g., 3.12 moles) in chloroform (1194 g., 10.0 moles), maintained at 0–5° under nitrogen, was added potassium *t*-butoxide[11] (700 g., 3.74 moles) for a period of 5 hr. The reaction mixture was drowned in water and the pH adjusted to 7. The clear amber organic phase was dried over sodium sulfate and distilled through a 1.5-ft. glass-helix packed column to remove *t*-butyl alcohol, chloroform, and most of the unchanged norbornylene. Further distillation at 0.5–0.8 mm. gave 84 g., b.p. 52–63° ($n^{20.5}$D 1.5262–1.5357), corresponding to a 15% yield of product. The center fraction, 54 g., had b.p. 53–59° and $n^{20.5}$D 1.5342–15352. The forerun, b.p. 33–52°, had a strong 5.75-μ band but was not investigated further.

Preparation of 8,8-Dichlorobicyclo[4.1.0]octane.—A solution of cycloheptene (102 g., 1.06 moles) in chloroform (476 g., 4.00 moles) was stirred under nitrogen and the temperature maintained at 0–5° for 1.5 hr. during which potassium *t*-butoxide mono-*t*-butylate[11] (238 g., 1.25 moles) was added. The mixture was warmed to room temperature, washed with water, and dried over sodium sulfate. Distillation gave 81 g., 43% yield of product, b.p. 50–53° (1 mm.), n^{20}D steady at 1.5028. Less than 1 g. of residue remained.

Preparation of 6,6-Dichlorobicyclo[3.1.0]hexane.—A freshly prepared solution of potassium (83 g., 2.11 g.-atoms) in *t*-butyl alcohol (2385 g.) was stripped until a slush remained and then 750 ml. of benzene was added. The slurry was stripped until 810 ml. distilled, cooled to 5°, and cyclopentene (204 g., 3.00 moles) in benzene (150 ml.) was added. Chloroform (298 g., 2.50 moles) was added over a 100-min. period such that the temperature was 13–15°. The neutral reaction mixture was washed with water and the organic layer dried and distilled through a 2.5-ft. Vigreux. The forerun gave 144 g., b.p. 42–45°, of cyclopentene. After removal of benzene and *t*-butyl alcohol, 125 g. of product, b.p. 68–93° at 20 mm., was obtained, corresponding to a 94% yield on cyclopentene converted and a 39% yield based on potassium. The main fractions centered around 69° at 20 mm. (62 g.) and 90° at 20 mm. (63 g.). The first fraction was shown to be 6,6-dichlorobicyclo[3.1.0]hexane (no double bond in the infrared, no reaction with sodium iodide in acetone at 50°, precipitate of silver chloride at 25° at a measurable rate with 0.1 *N* silver nitrate in ethanol, and n.m.r. consistent with bicyclic structure). The high boiling fraction was shown to be 2,3-dichlorocyclohexene (*vida supra* and Tables II and IV). It was unsaturated (infrared, potassium permanganate), gave an immediate precipitate with 0.1 *N* silver nitrate in ethanol and reacted at a measurable rate with 1 *M* sodium iodide in acetone and 2 *M* potassium hydroxide in methanol at 25–40°. Its n.m.r. spectrum had three hydrogens (6:1:1) with chemical shifts consistent with the structure assigned (δ 5.7 for vinyl hydrogen and δ 4.5 for CHCl hydrogen).

In order to determine whether the high boiling isomer was formed during the reaction or distillation a similar experiment was run. Potassium *t*-butoxide (896 g. of 60% material, 4.80 moles) was added to cyclopentene (400 g., 5.88 moles) in chloroform (1790 g., 15 moles) maintained at 5° over a 3-hr. period and the product worked up by washing with 2 l. of water followed by distillation of all volatiles to a head temperature of 77° at 1 atm. The clean residue showed only a trace of 2,3-dichlorocyclohexene (infrared). Nonetheless, distillation at 40 mm. gave 377 g. total of both products, b.p. 79–103° in 52% yield based on potassium *t*-butoxide. The ratio of the low to high boiling fractions (b.p. 80° and 98° at 40 mm.) in this experiment was about 2.7.

Thermal Rearrangement of 6,6-Dichlorobicyclo[3.1.0]hexane.—As a typical example of the thermal rearrangement reactions previously described 39 g. of the subject compound was heated for 5.5 hr. under nitrogen (2 hr. at reflux). Samples were tapped at hourly intervals and showed a gradual increase in n^{25}D to 1.5140[12] and the appearance of positive potassium permanganate and silver nitrate tests. The appearance of 2,3-dichlorocyclohexene also was followed in the infrared.

Distillation gave 39 g., b.p. 81–83° (15 mm.), corresponding to 100% yield of 2,3-dichlorocyclohexene.

Silver Nitrate Rearrangement of 6,6-Dichlorobicyclo[3.1.0]hexane.—A solution of 45 g., 0.30 mole, of compound in 400 cc. of 50% aqueous dioxane was treated with 93 g., 0.547 mole, of silver nitrate. The mixture was stirred at room temperature for 25.5 hr. and filtered to give 45 g. of silver chloride (105% yield). The organic material was isolated by ether extraction, drying, and distillation. The crude product, 7 g., had b.p. 86–87° (15 mm.), n^{22}D 1.5100. It gave a phenylurethan, m.p. 83.0–83.2°, mixed with authentic phenylurethan of 2-chloro-3-hydroxycyclohexene, m.p. 83.0–83.7°.

Reaction of 2,3-Dichlorocyclohexene with Silver Nitrate.—A solution of 21.4 g., 0.125 mole, of silver nitrate of water in 30 ml. of water and 25 ml. of tetrahydrofuran was mixed with 8.60 g., 0.0570 mole, of the subject dichloride. An immediate heavy precipitate came down and seemed to be complete in a few minutes. Fifty milliliters of water was added and the mixture stirred for 6 hr. after which it was diluted with 400 cc. of water, and ether was extracted. Titration showed that 0.053 mole of silver ion was consumed (93% of theory) and 7.70 g., 0.0536 mole, of silver chloride was recovered (94%).

Distillation of the ether extract gave 3.20 g. of product, b.p. 88–92° (16 mm.), n^{25}D 1.5067–1.5087, corresponding to a 42% yield of 2-chloro-3-hydroxy-cyclohexene. A higher boiling fraction, 1.25 g., b.p. 110–112° (16 mm.), and a residue of 1.2 g. were not investigated further.

A phenylurethan, m.p. 83.0–84.0, compares well with the literature value, 85–86°.[13]

Hydrogenation of 3,4-Dichlorobicyclo[3.2.1]octene-2.—A solution of 7.200 g., 0.0406 mole, of compound in 75 ml. of purified tetrahydrofuran was mixed with 5.288 g. of 5% palladium–charcoal (Baker) and 100 ml. of 1.000 *N* sodium hydroxide. The mildly exothermic hydrogenation took place at 25° (3 atm.) giving 35% uptake in 9 min., 76% in 26 min., and 90% in 343 min.

The catalyst was filtered off and washed with two 25-ml. portions of the tetrahydrofuran followed by five 100-ml portions of water. The combined filtrates were back titrated with hydrochloric acid. A total of 78.9 meq. of hydrochloric acid was produced (97% of theory). Ether extraction of the filtrates, drying, and distillation left 3.2 g., 71% yield of bicyclo[3.2.1]-octane which crystallized in part on cooling. Sublimation at 65–70° (1 atm.) gave several fractions, m.p. 131–133.5°, 134.5–135.3°, and 134.0–135.2°, all having perfect analyses for C_8H_{14}. The sublimation residue, 1.0 g., was impure product (contained 3.3% chlorine). The bicyclooctane is an extremely volatile solid.

Hydrolysis of 3,4-Dichlorobicyclo[3.2.1]octene-2.—A suspension of 6.0 g., 0.034 mole, of compound, 10 g., 0.10 mole, of calcium carbonate, and 15 g. of water was refluxed under nitrogen for 26 hr. The clean mixture was then extracted and the ether dried. The aqueous layer contained 0.0328 equiv. of chloride ion (96.5% yield). Distillation of the ether layer gave 4.2 g., 79% yield, of product, b.p. 67–75° (1 mm.). The product was similar to the chloro alcohol obtained by reaction of 3,4-dichlorobicyclo[3.2.1]octene-2 with silver nitrate (infrared). Its n.m.r. (δ vinyl hydrogen, 6.0; J = 7.0 c.p.s.; δ CHOH, 3.7; J = 2.5 c.p.s.; OH shifted upfield on dilution with carbon tetrachloride) compared well with that of the starting material (δ vinyl hydrogen, 6.1; J = 7.0 c.p.s.; δ CHCl, 4.2; J = 2.5 c.p.s.).

A phenylurethane of the product had m.p. 82.0–82.8°.

Reaction of 3,4-Dichlorobicyclo[3.2.1]octene-2 with Aqueous Silver Nitrate in Tetrahydrofuran.—A solution of 43.5 g., 0.256 mole, of silver nitrate in 75 ml. of water plus 100 ml. of tetrahydrofuran was mixed with 22.65 g., 0.128 mole, of the subject allylic chloride. An immediate heavy precipitate formed and was complete in less than 0.5 hr. After standing in the dark for a week the mixture was filtered, the filtrate diluted with water, and ether extracted. Titration of the aqueous layer showed that 0.120 mole of silver nitrate was consumed (94% of theory) and, correspondingly, 17.33 g., 0.121 mole, of silver chloride was isolated (94% of theory).

Distillation of the dried ether extract gave 14.5 g., 71.5% yield, of 3-chloro-4-hydroxybicyclo[3.2.1]octene-2, b.p. 70–75° (1 mm.), n^{20}D 1.5300–1.5280, and left 4.5 g. of residue.

Hydrogenation of 3-Chloro-4-hydroxybicyclo[3.2.1]octene-2.—A solution of 1.149 g. of chloro alcohol in 50 ml. of pure tetrahydrofuran and 25.00 ml. of 1.000 *N* sodium hydroxide was hydrogenated over 1.32 g. of 5% palladium–charcoal as described previously at 25° (3 atm.). The hydrogen uptake was 43% in 5 min. and 99% in 21 min. The theoretical amount of hydrogen chloride was produced. Work-up as before left 440 mg., 48% yield, of crude bicyclooctanol which on sublimation at 140° (1

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(11) City Chemical Co. material, *ca.* 60% active 40% *t*-butyl alcohol.

(12) Pure 2,3-dichlorocyclohexene has n^{25}D 1.5139 and b.p. 90° (20 mm.) (Table IV and ref. 5).

(13) Ref. 5.

atm.) gave fine needles, m.p. 191–192.5°. The phenylurethan of the volatile 2-hydroxybicyclo[3.2.1]octane was prepared by treating 50 mg. of phenyl isocyanate with 32 mg. of compound in 0.2 ml. of carbon tetrachloride. It had m.p. 127.5–128.0°.

Tests for S_N1 and S_N2 Reactivity.—The relative reactivity of the dichlorocarbene adducts and rearranged products was measured by their rates of reaction at room temperature with 0.1 *N* silver nitrate in ethanol, 1 *M* sodium iodide in acetone, and 15% potassium hydroxide in methanol (at 100°).

Acknowledgment.—The author is indebted to Dr. C. A. Reilly, of these laboratories, for the n.m.r. spectra and their interpretation.

Ring Expansion of 2-Alkyl-1-indanones to Isocarbostyril Derivatives[1]

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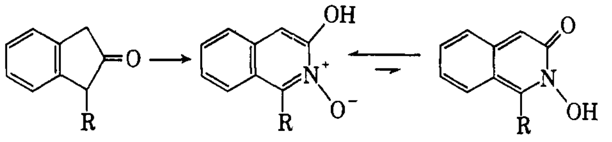
The nitrosation of 2-alkyl-1-indanones (4) under acid conditions leads to ring-expanded 2-hydroxy-3-alkylisocarbostyrils (6) in good yields *via* isolable precursors, the 2-alkyl-2-nitroso-1-indanones (5). The structure of 6 is confirmed by (i) independent synthesis–ozonization of 3-alkylisoquinoline 2-oxides (7); (ii) reduction of 6 to known 3-alkylisocarbostyril derivatives (8); and (iii) n.m.r. Tentative mechanisms for the ring expansions, 4 to 6 under strongly acid conditions and 5 to 6 in either base or acid media, are proposed.

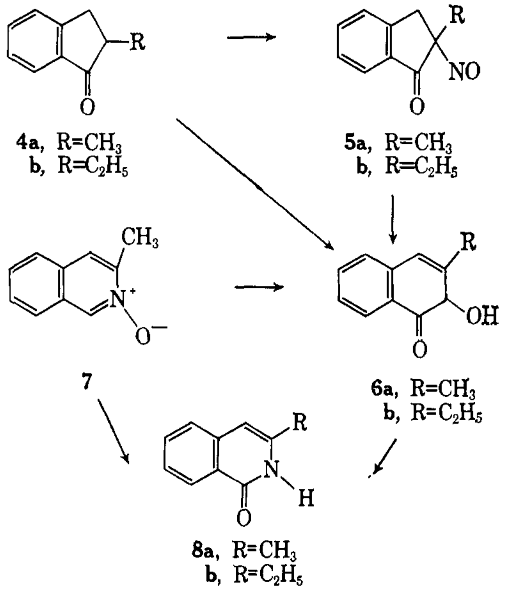
Our adventitious discovery that nitrosation of 1-alkyl-2-indanones (1) under alkaline conditions gave ring-expanded products tentatively formulated as 1-alkyl-3-hydroxyisoquinoline 2-oxides (2), or their energetically less favorable isoquinolone tautomers (3), has been reported recently.[2,3] Proof of structure of these cyclic hydroxamic acids has to date proven elusive. The postulated ring expansion, however, seemed to be in striking accord with the independent observations of Huebner and Kuehne in the nitrosation of isomeric 2-ethyl-1-indanone under acidic conditions.[4]



1a, R = CH_3
b, R = $CH_2OCH_2C_6H$ 2 3

In this communication we wish (i) to report that addition of *n*-butyl nitrite to a 1:1 molar equivalent of 2-alkyl-1-indanone–hydrochloric acid mixture produced 2-hydroxy-3-alkylisocarbostyrils (6) in good yield, and (ii) to provide unequivocal evidence for this novel ring expansion. Moreover, with lower acid concentration, and reversal of the mode of addition (acid to indanone–nitrite mixture), the stable precursors, 2-alkyl-2-nitroso-1-indanones (5), may be isolated. The over-all reaction sequence is shown in the diagram (col. 2).

Thus addition of excess *n*-butyl nitrite in toluene to a solution of 2-methyl-1-indanone (4a)/2-ethyl-1-indanone (4b) in toluene and 3 *N* hydrochloric acid in ethyl acetate at 0° produced, after four days, 2-hydroxy-3-methyl-isocarbostyril (6a)/2-hydroxy-3-ethylisocarbostyril (6b) in 65–68% yields. Similar reaction conditions, but a shorter reaction time, converted 4a to the expected mixture of 5a (6%) and 6a (45%).



Further, the addition of several drops of concentrated hydrochloric acid to an ice-cooled solution of 4a/4b and *n*-butyl nitrite in benzene gave a blue solution from which precipitated 2-methyl-2-nitroso-1-indanone (5a)/2-ethyl-2-nitroso-1-indanone (5b) in 61% yield. Upon increasing the acid concentration, but with identical reaction conditions, 4a was converted to a mixture of 5a (40%) and 6a (12%). 5a isomerized to 6a rapidly in refluxing methanolic sodium methoxide solution and slowly in concentrated hydrochloric acid.

Threefold confirmation of the structure of the ring-expanded 6a was achieved in the following manner.

(i) 6a was independently synthesized in 15% yield *via* ozonization of 3-methylisoquinoline 2-oxide (7) in methylene chloride at 0° with one molar ozone equivalent.[5] The physical and chemical identity of the cyclic hydroxamic acid product 6a produced by both ring expansion and ozonization are indisputable. Thus, for example, each, on treatment with benzoyl chloride in pyridine–aqueous sodium carbonate, gave identical N-benzoate esters.

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(2) A. T. Blomquist and E. J. Moriconi, *J. Org. Chem.*, **26**, 3761 (1961).

(3) The rearrangement did not occur in acid media.

(4) Private communication from C. F. Huebner and M. E. Kuehne, Ciba Pharmaceutical Products, Inc.

(5) The scope of this ozonization reaction has been reported at the N. Y.–N. J. Metropolitan Regional Meeting of the American Chemical Society, January 22, 1962, and at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1962.