Addition Products of Dichlorocarbene to Norbornylene and Norbornadiene and Their Rearrangements[1]

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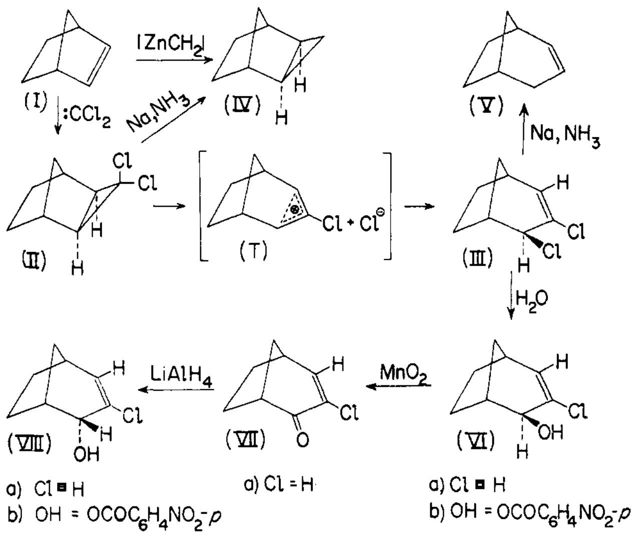
Received March 4, 1963

The addition of dichlorocarbene to norbornylene yielded 3,3-dichloro-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane (II) which rearranged with great facility to *exo*-3,4-dichlorobicyclo[3.2.1]oct-2-ene (III). The nuclear magnetic resonance spectra allowed configurational assignments and are presented in detail. The rearrangement of II to III exhibited first-order kinetics at 22° when carried out in carbon tetrachloride, methylene chloride, acetone, and acetonitrile, the rate being strongly affected by the dielectric constant of the solvent. Preliminary observations on the less clear-cut reaction of dichlorocarbene with norbornadiene are reported.

Preliminary to a study of the addition of carbenes[3] to systems[4] capable of undergoing rearrangement during or subsequent to addition, we have examined a model which was expected to reflect the classical stereospecific addition of dihalocarbenes to olefins.[5] Indeed, 3,3-dichloro-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane (II) was the only product detected upon treatment of norbornylene (I) with dichlorocarbene. The nuclear magnetic resonance (n.m.r.) spectrum[1] of this substance is tabulated in Table I and shown in Fig. 1. The following features of the n.m.r. spectrum strongly support the assignment of the *exo*-configuration to the molecule. The methylene protons at carbon-8 showed a spectacular reaction to the environmental differences provided by the close proximity of the *gem*-dichloro function. Their absorptions appeared at 9.24 and 7.86 τ with a coupling constant of 10.9 c.p.s., as opposed to the closely grouped, more normal positions of the ethylene-bridge proton absorptions at 8.68 and 8.48 τ. Furthermore, the sharp singlet at 8.39 τ assigned to the protons at the cyclopropane fusion is also consistent with this geometry.[7]

Chart I



Direct chemical evidence for the structural assignment of II was obtained by its reduction with sodium in liquid ammonia to the known tricyclo[3.2.1.$0^{2,4}$]octane (IV).[8] The *exo*-configuration of IV as prepared by the Simmons–Smith procedure[8] can now be considered to be experimentally confirmed, and hence it no longer rests upon the previous semi-intuitive method of assignment.[8] It should be noted in this regard that the n.m.r. spectrum of IV is very difficult to interpret since there is much overlap in the absorptions.

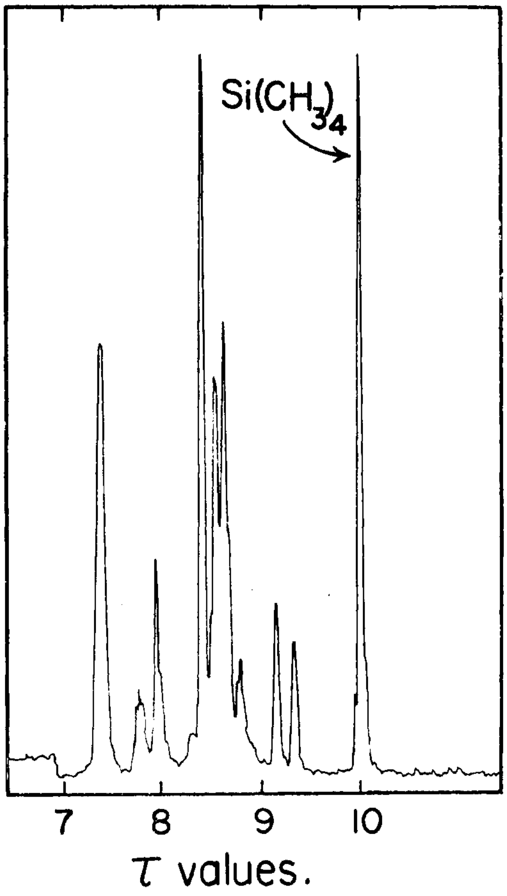


Fig. 1.—N.m.r. spectrum of 3,3-dichloro-*exo*-tricyclo[3.2.1.$0^{2,4}$]-octane.

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[1] Communication no. 2347 from the Kodak Research Laboratories.

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[3] For recent reviews with leading references, see: W. Kirmse, *Angew. Chem.*, **73**, 161 (1961); R. C. De Selms, "Organic Chemical Bulletin," **34**, No. 1 (1962) (published by the Research Laboratories of the Eastman Kodak Co.).

[4] H. Kwart and W. G. Vosburgh, *J. Am. Chem. Soc.*, **76**, 5400 (1954) and previous papers by Kwart; S. Winstein and M. Shatavsky, *Chem. Ind.* (London), 56 (1956).

[5] P. S. Skell and G. Y. Garner, *J. Am. Chem. Soc.*, **78**, 3409 (1956); W. von E. Doering and W. A. Henderson, Jr., *ibid.*, **80**, 5274 (1958).

[6] N.m.r. spectra were obtained from carbon tetrachloride solutions (unless otherwise noted) on the Varian Associates HR-60 spectrometer. Tetramethylsilane was used as an internal reference in all samples.

[7] H. E. Simmons, *J. Am. Chem. Soc.*, **83**, 1657 (1961).

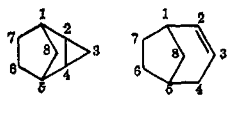
[8] H. E. Simmons and R. D. Smith, *ibid.*, **81**, 4256 (1959); *cf.* K. B. Wiberg and W. J. Bartley, *ibid.*, **82**, 6375 (1960).

TABLE I

N.M.R. SPECTRAL DATA

Compound	Chemical shift, τ	Relative area	Multiplicity	Coupling constant, sec.$^{-1}$	Assignment, (position of proton attachment[a])
IV	7.79	2	1 (broad)		1,5
	8.48 9.55 (limits)	8	Complex		2,4,6,7,8
	9.75	1	Complex (5)		3
	10.24	1	Complex (4)		3
II	7.37	2	1 (broad)		1,5
	8.39	2	1		2,4
	8.48	2	2	9.7	6,7
	8.68	2	2		
	7.86	1	6	10.9	8
	9.24	1	6	10.9	8
X	3.46	2	3	1.7	6,7
	6.80	2	1 (broad)		1,5
	7.65	1	6	9.9	8
	9.00	1	6		
	8.19	2	2	0.9	2,4
V	4.18	1	Complex (3)		2,3
	4.83	1	Complex (2)		
	7.72	2	1 (broad)		1,5
	7.71 9.01 (limits)	8	Complex		4,6,7,8
III	3.92	1	4	7.1 1.0[c]	2
	5.89	1	2	2.8	4
	7.28	1	1 (broad)		1,5
	7.35	1	1 (broad)		
	7.81 8.80 (limits)	6	Complex		6,7,8
VI	6.33	1	2	2.9	4
VIa[b]	6.33	1	2	2.8	4
VIb	4.90	1	2	2.8	4
VIII	5.63	1	2	4.6	4
VIIIa	5.58	1	2	4.3	4
VIIIb	4.18	1	2	4.5	4
XI	3.43	1	4	5.6	6,7
	4.14	1	4	3.0	
	3.66	1	2	6.8	2
	5.87	1	2	1.8	4
	6.86	1	1 (broad)		1,5
	7.14	1	1 (broad)		
	7.90	2	Complex		8
XII	3.80	1	4	5.5	6,7
	4.25	1	4	2.8	
	3.94	1	6	7.3 1.4	2
	7.11 8.37	6	Complex		1,4,5,8

[a] The following numbering systems are used:



[b] D$_2$O added. [c] This is apparently a transannular coupling.

In retrospect, it is amazing that II was isolated at all since molecular models[9] indicate a high degree of crowding for this structure. In accord with this high degree of strain, it was found that a very delicate method was necessary in the isolation (see Experimental) and, also, that II readily rearranged to the less strained *exo*-3,4-dichlorobicyclo[3.2.1]oct-2-ene (III). In similar experiments[10] the apparently much less stable adduct of dibromocarbene and norbornylene corresponding to II was not even detected and only the rearranged isomer corresponding to III was obtained. Similar rearrangements of other fused *gem*-dihalocyclopropanes have been reported recently.[11]

Chemical confirmation of the nuclear structure of III was provided by its reduction with sodium in liquid ammonia to the known bicyclo[3.2.1]oct-2-ene (V).[10,12] The other aspects of its structure were consistent with its n.m.r. spectrum (see Table I and Fig. 2). How-

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[9] Molecular models consulted by these authors were of the Dreiding, Courtauld, and "ball-and-spring" varieties.

[10] (a) W. R. Moore, private communication; (b) C. W. Jefford, *Proc. Chem. Soc.*, 64 (1963); (c) E. Bergman, abstracts of papers presented at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1962, p. 79 (in the case of dichlorocarbene); (d) H. Ghosez and P. Laroche, *Proc. Chem. Soc.*, 90 (1963).

[11] E. Vogel, *Angew. Chem.*, **73**, 548 (1961); J. Sonnenberg and S. Winstein, *J. Org. Chem.*, **27**, 748 (1962).

[12] A. F. Bickel, J. Knotnerus, E. C. Kooyman, and G. C. Vegter, *Tetrahedron*, **9**, 230 (1960).

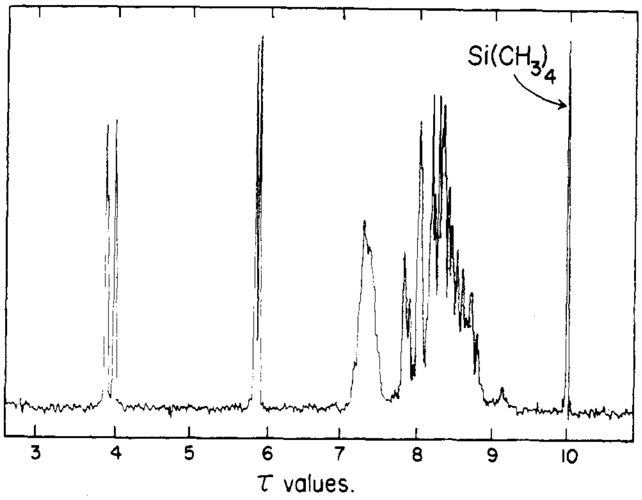

Fig. 2.—N.m.r. spectrum of *exo*-3,4-dichlorobicyclo[3.2.1]oct-2-ene.

ever, the coupling constant of the proton at carbon-4 ($J_{4,5}$ = 2.8 c.p.s.) of III would not allow unambiguous assignment of configuration at that carbon by comparison with the values of 0.3 and 5.5 c.p.s. estimated for the *exo*- and *endo*-configurations, respectively, using molecular models[9] and the results of Karplus[13] and Anet.[14] The lack of agreement between measured coupling constant and that calculated for the structure on the basis of the Karplus[13] relationship is not surprising. Although Anet[14] did obtain good agreement in the case of camphene-2,3-diols, agreement has not always been observed by others.[15] As pointed out by Meinwald and Lewis, the lack of agreement serves to emphasize the limitations of the Karplus theory. At the same time, limitations of the models must not be overlooked.

In order to establish the configuration of III at carbon-4, we decided to examine the n.m.r. coupling constants of model systems where both epimers were known. *exo*-4-Hydroxybicyclo[3.2.1]oct-2-ene (VIa) was prepared by a known route[16] and had $J_{4,5}$ = 2.8 c.p.s. Compound VIa was converted *via* the ketone VIIa to the epimeric *endo*-alcohol VIIIa by the method of Goering, Greiner, and Sloan.[17] The coupling constant, $J_{4,5}$, in VIIIa was found to be difficult to measure because of coupling of the carbon-4 proton with the proton at carbon-3. It was tentatively assigned a value of 4.3 c.p.s.

All ambiguity was removed by examination of the actual series being investigated. Compound III was hydrolyzed in refluxing acetone–water to the corresponding *exo*-allylic alcohol VI, which had $J_{4,5}$ = 2.9 c.p.s. Proceeding as before, through the ketone VII to the epimeric *endo*-alcohol VIII with $J_{4,5}$ = 4.6 c.p.s., provided the final evidence that III must have the *exo*-configuration. It should be noted that the *exo*-configuration should be energetically preferred in this molecule since the bulky chloro function in this position is opposed to the methylene bridge, whereas, in the *endo*-configuration it would be opposed to the larger ethylene bridge.

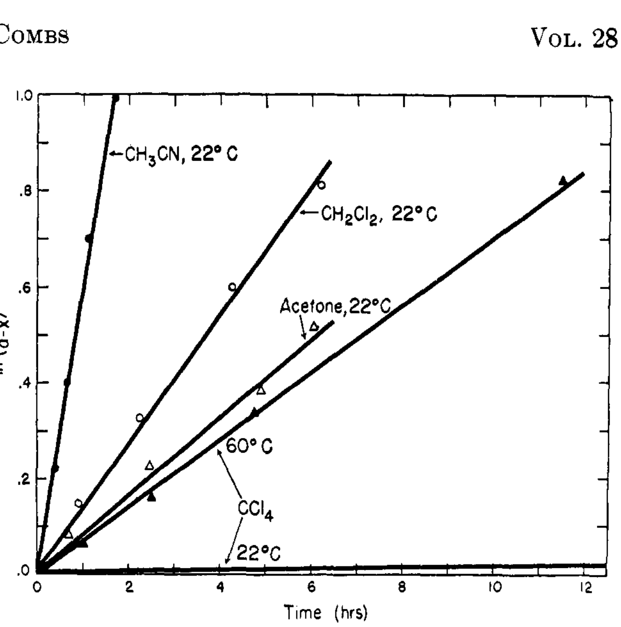

Fig. 3.—First-order plot for rearrangement of 3,3-dichloro-*exo*-tricyclo[3.2.1.0^{2,4}]octane to *exo*-3,4-dichlorobicyclo[3.2.1]-oct-2-ene.

The fact that there is such a small variation in the coupling constants of the protons at carbon-4 in the derivatives of V that we have examined should provide a positive method for assigning configurations in other members of this series and other substituents (*cf.* earlier methods as discussed in ref. 17).

Kinetics Data

At the time we first observed the rearrangement of II to III, we could find no examples reported in the literature of this type of rearrangement occurring with retention of halide, although many examples had been reported at high temperatures with concomitant loss of hydrogen halides and in media where the halide was displaced.[18,19] Rearrangements of *gem*-dihalocyclopropanes apparently had been found to be of both ionic[12,18,19] and free radical[20] nature. It was, therefore, considered of interest to establish some of the gross aspects of the rearrangement mechanism by a preliminary kinetics survey.

The rearrangement occurred at a convenient rate for study. It was easily followed by observing the disappearance of the absorption of II at 9.24 τ from one of the protons on carbon-8 and the simultaneous appearance of the absorptions of III at 3.92 and 5.89 τ due to the protons on carbon-2 and -4. First-order kinetics were observed for the rearrangement in the four solvents studied at 22° and also for the carbon tetrachloride solution at 60° (see Fig. 3).

The strong effect on the rate of reaction of the dielectric constant of the solvent (Table II) was considered to be indicative of an ion-pair intermediate (*i.e.*, T) being formed in the rate-determining step[21] with rapid conversion to III. From the data obtained,

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[13] M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

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

[15] J. Meinwald and A. Lewis, *J. Am. Chem. Soc.*, **83**, 2769 (1961); R.V. Lemiaux, J. D. Stevens, and R. R. Fraser, *Can. J. Chem.*, **40**, 1955 (1962.)

[16] R. R. Sauers, *Tetrahedron Letters*, No. **4**, 146 (1961); P. Nedenskov, H. Heide, and N. Clausen-Kaas, *Acta Chem. Scand.*, **16**, 246 (1962).

[17] H. L. Goering, R. W. Greiner, and M. F. Sloan, *J. Am. Chem. Soc.*, **83**, 1391 (1961).

[18] E. E. Schweizer and W. E. Parham, *ibid.*, **82**, 4085 (1960); and previous papers by Parham.

[19] P. S. Skell and S. R. Sandler, *ibid.*, **80**, 2024 (1958).

[20] N. P. Neureiter, *J. Org. Chem.*, **24**, 2044 (1959).

[21] Although dielectric constant appears to be a major factor affecting the rate constant, the result for acetone indicates that it is not the only factor.

TABLE II

RATE CONSTANTS FOR REARRANGEMENT REACTIONS

Solvent	Dielectric constant	Temperature, °C.	First-order rate constant, sec.$^{-1}$
CCl_4	2.24	22 ± 0.5	2.78×10^{-7}
		60 ± 1	1.98×10^{-5}
CH_2Cl_2	9.08	22 ± 0.5	3.87×10^{-6}
$(CH_3)_2CO$	21.4	22 ± 0.5	2.32×10^{-5}
CH_3CN	38.8	22 ± 0.5	1.62×10^{-4}

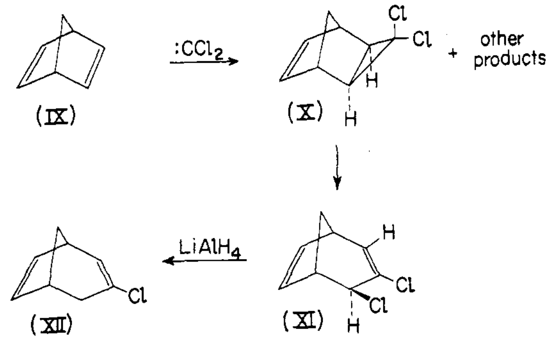
no conclusion can be drawn concerning the precise nature of T (*i.e.*, bridged ion, etc.) or whether or not the epimeric *endo*-3,4-dichlorobicyclo[3.2.1]oct-2-ene might have participated.

Although from these data we believe it highly improbable that this rearrangement might have a radical component, we nevertheless investigated one such possibility. It was found that the rearrangement did not proceed in any different manner at 60° with added benzoyl peroxide in carbon tetrachloride.

Addition of Dichlorocarbene to Norbornadiene[22]

Treatment of norbornadiene (IX) with dichlorocarbene did not give such clear-cut results as the previous example. Examination of the total product by vapor phase chromatography indicated the presence of not less than six substances. These substances distilled in a narrow range [70–85° (4.4–4.5 mm.)], indicating that they are probably isomeric. The component present in the largest amount was concentrated by low-temperature distillation to about 90% purity, but refinement to a greater degree was not found possible in our hands. This substance was 3,3-dichloro-*exo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene (X), as indicated by its n.m.r. spectrum and its facile conversion on standing to *exo*-dichlorobicyclo[3.2.1]octa-2,6-diene (XI). The *exo*-configurations were inferred by comparisons of the n.m.r. spectra with those of the corresponding products II and III from norbornylene. The allylic nature of the 4-chloro substituent in XI was demonstrated by its ready hydrogenolysis with lithium aluminum hydride,[23] yielding 3-chlorobicyclo[3.2.1]octa-2,6-diene (XII).

CHART II



Although we have reason to believe that the rearrangements of II to III and X to XI are stereospecific, our present data do not allow this conclusion to be drawn.

Experimental[24]

3,3-Dichloro-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane (II).—To a mixture of 28.2 g. (0.30 mole) of norbornylene, 33.6 g. (0.30 mole) of potassium *t*-butoxide, and 200 ml. of *n*-pentane at 0° was added 35.7 g. (0.30 mole) of chloroform in small portions. The mixture was stirred for 1 hr. at room temperature, poured into an equal volume of water, the resulting mixture was extracted with pentane, the extract dried over magnesium sulfate, the solvent removed at low pressure and low temperature (<35°), and the residue distilled. One fraction was obtained, 2.00 g. (3.8% of theoretical), which distilled at 44.0–45.5° (0.7 mm.); n^{25}_D 1.5209; d^{20}_4 1.250. The forerun and residue contained no other product by vapor phase chromatography examinations.

Anal. Calcd. for $C_8H_{10}Cl_2$: C, 54.3; H, 5.7; Cl, 40.0; mol. wt., 177. Found: C, 54.7; H, 5.6; Cl, 40.1; mol. wt., 177.

The yield was increased to 25.2% of the theoretical by utilizing sodium methoxide and ethyl trichloroacetate for the generation of dichlorocarbene.[25]

***exo*-3,4-Dichlorobicyclo[3.2.1]oct-2-ene (III).**—When 3,3-dichloro-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane (II) was allowed to stand at room temperature or below, it was slowly converted to III (see Kinetics Data). This conversion was accelerated to completion by heating II at temperatures above 100° for several hours. Compound III distilled at 51° (0.3 mm.); n^{25}_D 1.5333; d^{20}_4 1.250.

Anal. Calcd. for $C_8H_{10}Cl_2$: Cl, 40.0; mol. wt., 177. Found: Cl, 40.2; mol. wt., 177.

***exo*-Tricyclo[3.2.1.$0^{2,4}$]octane (IV).**[8]—To 32.6 g. (0.50 mole) of zinc, treated as described by Shank and Schechter[26] in 325 ml. of ether, was added 107.2 g. (0.40 mole) of diiodomethane and 0.3 g. of iodine (catalyst). The mixture was refluxed for 30 min., 37.5 g. (0.40 mole) of norbornylene in 50 ml. of ether was added dropwise over a 10-min. period, and the refluxing was continued for 48 hr. The mixture was filtered through Celite, the filtrate was washed successively with 5% aqueous hydrochloric acid, saturated sodium bicarbonate solution and water, and dried over magnesium sulfate. Removal of solvent left 45 g. of product which was distilled at atmospheric pressure. The material boiling at 132–150° (9.4 g., 22% of theoretical, n^{25}_D 1.4767) was 99% pure by vapor phase chromatography. The literature[8] gives b.p. 136–137°, n^{25}_D 1.4778.

This same compound was prepared by treatment of 3,3-dichloro-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane (II) with sodium in liquid ammonia.

Bicyclo[3.2.1]oct-2-ene (V).—In an inert atmosphere, 5.00 g. (0.028 mole) of *exo*-3,4-dichlorobicyclo[3.2.1]oct-2-ene (III) in 40 ml. of anhydrous ether was added gradually, in 1.25 hr., to a solution of 12.4 g. (0.54 g. atom) of sodium in 100 ml. of liquid ammonia. The ammonia was allowed to evaporate in 3 hr., while 100 ml. of ether was added. The excess sodium and sodium amide were decomposed by cautious addition of a solution of 20 ml. of methanol in 200 ml. of ether, then pure methanol, and finally water. The organic layer was separated, washed with water, and dried over magnesium sulfate. Removal of the solvent yielded 1.30 g. of product (85% pure by vapor phase chromatography; 36% of theoretical) which was distilled at 90–110° and repeatedly sublimed onto a cold finger at 40° (760 mm.) to a constant melting point of 37.5–38.0° (cor.) (sealed capillary). This product is extremely volatile.

Anal. Calcd. for C_8H_{12}: C, 88.8; H, 11.2. Found: C, 89.2; H, 11.4.

3-Chloro-4-*exo*-hydroxybicyclo[3.2.1]oct-2-ene (VI).—A solution of 23.24 g. (0.131 mole) of *exo*-3,4-dichlorobicyclo[3.2.1]-oct-2-ene (III), 500 ml. of acetone, and 250 ml. of water was heated at reflux for 24 hr., treated with 36.2 g. (0.262 mole) of potassium carbonate, and extracted continuously for 24 hr. with ether containing a little pentane. The extract was dried over magnesium sulfate and distilled at reduced pressure, yielding 18.27 g. (88%) of product, b.p. 66–68° (0.05 mm.). Fortuitous circumstances led to the crystallization of this product, and

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[22] *Cf.* the results of J. A. Yankeelov, Jr., *Dissertations Abstr.*, **20**, 3085 (1960).

[23] L. F. Hatch and R. H. Perry, Jr., *J. Am. Chem. Soc.*, **71**, 3262 (1949).

[24] Molecular weights were obtained by mass spectrometry. Boiling points were not corrected. Vapor phase chromatographic examinations were carried out on an 8-ft. glass column, of i.d. of 5 mm., containing 28% General Electric S.E. 30 silicone gum rubber on 80- to 100-mesh acidic and basic washed Celite 545. Infrared spectra were consistent with all structures assigned.

[25] W. E. Parham and E. E. Schweizer, *J. Org. Chem.*, **24**, 1733 (1959).

[26] R. S. Shank and H. Schechter, *ibid.*, **24**, 1825 (1959).

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, $n^{25}\text{D}$ 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.), $n^{25}\text{D}$ 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.), $n^{25}\text{D}$ 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.

Acknowledgment.—The authors wish to express their appreciation to Dr. O. E. Schupp, III, for vapor phase chromatography; Mr. G. P. Happ, for the mass spectrometry; and Mr. D. F. Ketchum, for the microanalyses; and to all of them for their collaboration with this work.

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Reactions Related to the Addition of Dichlorocarbene to Norbornylene

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Received June 25, 1962

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