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BICYCLANES—II[1]

ON THE PREPARATION AND HALOGENATION OF BICYCLO[2,2,2]OCTANE

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Abstract—In the presence of traces of acidic materials, Diels–Alder condensation of ethylene and cyclohexadiene-1,3 gives, besides the expected bicyclo[2,2,2]octene-2, the isomeric bicyclo[3,2,1] octene-2; the latter is formed through acid-catalysed rearrangement. Its structure was proved among other things by stepwise oxidative degradation to cyclopentane-*cis*-1,3-dicarboxylic acid.

Competitive halogenations of bicyclo[2,2,2]octane and cyclohexane showed that the methylene groups in the latter are somewhat more reactive. Reactivity ratios decreased at increasing temperatures.

The reactivity of the bridgehead positions in bicyclo-octane towards hydrogen removal is appreciably larger than that of the methylene groups, in contrast to the situation in bicyclo[2,2,1]-heptane. This is probably due to the greater flexibility of the bicyclo-octane skeleton permitting a near-planar configuration at the bridgehead. Some of the differences between the bicyclo[2,2,2]octane, bicyclo[2,2,1]heptane and cyclohexane systems are briefly discussed.

In Part I two of us[1] described the halogenation of bicyclo[2,2,1]heptane, using various free-radical methods. In continuation of this work the preparation and properties of bicyclo[2,2,2]octane were examined.

Model considerations suggest that this bicyclane has a rigid structure, while its bond angles are probably close to the tetrahedral values. It seemed of interest, therefore, to compare its properties with those of the also rigid but highly strained bicycloheptane.

Bicyclo[2,2,2]octane was synthesized by Alder and Stein, who started from cyclohexadiene-1,3 and acrolein;[2] the corresponding bicyclene was also first prepared by indirect methods, starting from cyclohexadiene-1,3 and ethyl acrylate.[3]

Walborsky and Loncrini were the first to report the direct synthesis of bicyclo-[2,2,2]octene-2 from cyclohexadiene-1,3 and ethylene;[4] the same reaction was reported independently by Hine *et al.*[5]

The chemical behaviour of bicyclo[2,2,2]octane does not seem to have been studied so far; several derivatives have been prepared by indirect methods, however, e.g. the 1- and 2-halides.[6–9]

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[1] Bicyclanes–I: E. C. Kooyman and G. C. Vegter, *Tetrahedron* **4**, 382 (1958). In the present article the nomenclature has been changed to conform with the I.U.P.A.C. rules.

[2] K. Alder and G. Stein, *Liebigs Ann.* **514**, 1 (1934).

[3] R. Scha and O. Tramposch, *Ber. Dtsch. Chem. Ges.* **75**, 1379 (1942).

[4] H. M. Walborsky and D. F. Loncrini, *J. Amer. Chem. Soc.* **76**, 5396 (1954).

[5] J. Hine, J. A. Brown, L. H. Zalhow, W. E. Gardner and M. Hine, *J. Amer. Chem. Soc.* **77**, 594 (1955).

[6] G. Komppa, T. Hirn, W. Rohrmann and S. Beckmann, *Liebigs Ann.* **521**, 242 (1936).

[7] W. von E. Doering and M. Farber, *J. Amer. Chem. Soc.* **71**, 1514 (1949).

[8] H. M. Walborsky, *Experientia* **9**, 209 (1953).

[9] Adnan Abdul-Rida Sayigh, Columbia University, New York City, Diss. 1952.

The present paper mainly deals with the preparation and halogenation of bicyclo-[2,2,2]octane, starting from the above direct synthesis of the bicyclene; in this reaction, an isomer appeared to be formed under acidic conditions, viz. bicyclo-[3,2,1]octene-2.

1. *Diels–Alder condensation of cyclohexadiene*-1,3 *and ethylene*

Bicyclo[2,2,2]octene-2, m.p. 112–113°, b.p. 134°, was prepared in a glass-lined autoclave according to Hine *et al.*[5] When an unlined steel autoclave was used, however, a different olefin having the same boiling point but melting at 43–45° was obtained as the main product; catalytic hydrogenation of this material yielded a bicyclooctane melting at 136–137·5° (the melting point of bicyclo[2,2,2]octane is 174°). Literature data on the melting points of bicyclo[3,2,1]octene and -octane suggested that the compounds prepared in the steel autoclave were the [3,2,1]-isomers. Conclusive evidence to this effect is presented in §2.

Bicyclo[3,2,1]octene has also been mentioned by von Braun and Reitz[10] but these authors probably obtained it in admixture with bicyclo[3,3,0]octene, since hydrogenation produced a liquid; pure bicyclo[3,2,1]octane melts at 141° (cf. Birch *et al.*[11]).

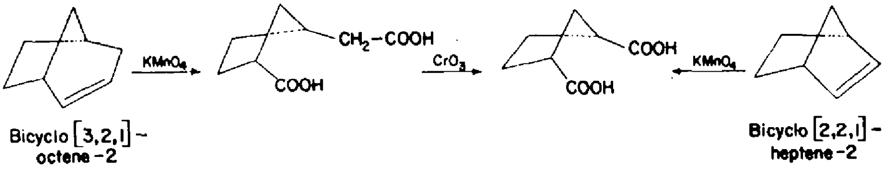
The above difference could be attributed to acid-catalysed isomerization of the normal Diels–Alder condensation product, since the addition of a small amount of pyridine led to the pure [2,2,2]-isomer even when an unlined steel autoclave was used. Moreover, the latter olefin could be rearranged to the [3,2,1]-isomer when heated to the reaction temperature of the Diels–Alder addition (250°) in the presence of moist ferric chloride in a glass-lined vessel; it appeared to be stable at this temperature in the absence of the catalyst.

Probably, our cyclohexadiene contained traces of organic bromides (e.g. bromocyclohexene) formed from the starting material dibromocyclohexane; these in turn produced some ferric bromide in the unlined steel vessel.

2. *Proof of structure of bicyclo*[3,2,1]*octene*-2 *by oxidative degradation*

Alder *et al.*, who prepared bicyclo[3,2,1]octene-2 along different routes, established its structure by ozonolysis.[12] We employed the following method:

Oxidation with potassium permanganate yielded a dicarboxylic acid $C_8H_{12}O_4$, which had been also obtained by Alder *et al.* upon ozonolysis of bicyclo[3,2,1]octene[12] as well as by oxidation of bicyclo[3,2,1]octanol-2.[13] Further oxidation of this acid by means of chromic acid in glacial acetic acid produced cyclopentane-*cis*-1,3-dicarboxylic acid, identical with a reference sample prepared by permanganate oxidation of bicyclo[2,2,1]heptene-2:



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[10] J. von Braun and J. Reitz, *Ber. Dtsch. Chem. Ges.* **74**, 273 (1941).

[11] S. F. Birch, R. A. Dean, N. J. Hunter and E. V. Whitehead, *J. Org. Chem.* **22**, 1590 (1957).

[12] K. Alder, H. Krieger and H. Weiss, *Chem. Ber.* **88**, 144 (1955).

[13] K. Alder and E. Windemuth, *Ber. Dtsch. Chem. Ges.* **71**, 2404 (1938).

Oxidation of bicyclo[2,2,2]octene-2 is reported[4] to yield cyclohexane-*cis*-1,4-dicarboxylic acid besides other products.

On hydration with 60 per cent sulphuric acid, bicyclo[3,2,1]octene gave the known bicyclo[3,2,1]octanol-2, which was also obtained by Newman and Tien Yu on hydration of bicyclo[2,2,2]octene-2.[14]

3. *Chlorination of bicyclo*[2,2,2]*octane*

Chlorination reactions were carried out in carbon tetrachloride solution at 30°, using molecular chlorine as the reagent and light as the initiating agent. Conversions were about 30 per cent.

Chlorination products could not be readily separated from the parent hydrocarbon by fractional distillation. Reaction mixtures were therefore analyzed by infrared and mass spectrometry after removal of the solvent. Spectroscopic standards used for both methods consisted of pure samples of (a) bicyclo[2,2,2]octane, (b) 2-chlorobicyclo[2,2,2]octane, prepared by addition of HCl to the corresponding bicyclene,[4,7,8] and (c) 1-chlorobicyclo[2,2,2]octane prepared via the 1-carboxylic acid according to Sayigh.[9]

Results are given in Table 1.

Thus in bicyclo-octane the two bridgehead positions are about equally reactive with regard to hydrogen abstraction as the six methylene groups, i.e. the tertiary hydrogens are about six times as reactive as those in secondary positions.

4. *Competitive halogenations of bicyclo*[2,2,2]*octane and cyclohexane*

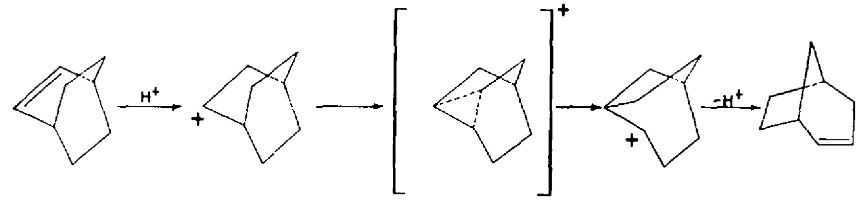
Equimolar amounts of the two hydrocarbons in carbon tetrachloride were reacted with molecular chlorine and bromine at 5° and at 80°. Conversions were about 10 per cent and ultra-violet light was the initiating agent. The products were analyzed by gas-liquid chromatography, which under our conditions failed to distinguish between the 1- and 2-halides of bicyclo-octane. Results are given in Table 2:

General trends appear to be similar for the two bicyclanes, relative reactivities being of the same order of magnitude and decreasing with increasing temperature.

DISCUSSION

1. *Isomerization of bicyclo*[2,2,2] *to* [3,2,1]*octene*-2 *and related reactions*

According to Walborsky[8] these rearrangements should proceed through an intermediate or transition state of the non-classical ion type (B), formation of which is preceded and/or followed by that of a classical ion (A, C). In terms of this concept, the isomerization of bicyclo[2,2,2]octene-2 may be described as follows:



Bicyclo [2,2,2]-octene-2

Classical [2,2,2]-2 ion(A)

Intermediate or transition state (B)

Classical [3,2,1]-2 ion(C)

Bicyclo [3,2,1]-octene-2

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[14] M. S. Newman and Y. Tien Yu, *J. Amer. Chem. Soc.* 74, 507 (1952).

TABLE 1. CHLORINATION OF BICYCLO[2,2,2]OCTANE

Products	Analysis*	
	Infra-red	Mass spectrometry
Bicyclo[2,2,2]octane	74% ± 5%	~70%
1-Chlorobicyclo[2,2,2]octane	16% ± 5%	~24%
2-Chlorobicyclo[2,2,2]octane	14% ± 5%	
Trichloro compounds		2-5%

* Mean values from several runs.

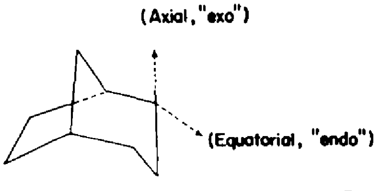
TABLE 2. COMPETITIVE HALOGENATIONS OF BICYCLO[2,2,2]OCTANE AND CYCLOHEXANE COMPARED WITH THOSE OF BICYCLO[2,2,1]HEPTANE AND CYCLOHEXANE

Halogenating agent	Temperature	Relative reactivities	
		$\frac{K_{b\text{(icyclo-octane)}}}{K_{c\text{(yclohexane)}}}$ (a)	$\frac{K_{b\text{(icycloheptane)}}}{K_{c\text{(yclohexane)}}}$ (b)
Cl_2	5°	0·96 ±0·05	0·99
Cl_2	80°	0·69 ± 0·03	0·79
Br_2	5°	3·1 ± 0·6	1·02
Br_2	80°	1·6 ± 0·2	0·55

(a) $K_b/K_c = \frac{\log(1 - (R_bCl)/(R_bH)_o)}{\log(1 - (R_cCl)/(R_cH)_o)}$, where $(R_bH)_o$ and $(R_cH)_o$ are the initial concentrations of the two hydrocarbons and (R_bCl) and (R_cCl) the final concentrations of the monohalides. Data given are mean values from at least four runs.
(b) cf. Part 1.[1]

Other examples of the rearrangement A → C are the isomerization of the bromide under the influence of silver bromide[7] and the acid-catalysed hydration of bicyclo-[2,2,2]octene-2[14] to give the same carbinol as the [3,2,1]bicyclene, viz. the type C alcohol.

Since these reactions are probably reversible, product compositions should be controlled by thermodynamics. In the derivatives of type A, substituents are necessarily in the crowded axial position; in the type C compounds, the six-membered ring has the chair conformation, which permits a substituent to occupy a favourable equatorial position (D):



Axial and equatorial directions in a 2-substituted bicyclo [3,2,1] octane (D)

Similarly, formation of the [3,2,1]bicyclene from the [2,2,2]-isomer should be due to the relieving of strain involved in the formation of a cyclohexene ring having the "half-chair" rather than the "half-boat" conformation; here, too, the equilibrium lies far towards the side of the [3,2,1]-isomer.

So far, no definite experimental data appear to be available as regards the geometry of the 2-substituted bicyclo[3,2,1]octanes. According to the above reasoning, the substituents should be in the equatorial positions, i.e. away from the methylene bridge.* It may be noted, however, that the solvolysis of bicyclo[2,2,1]heptyl-2 halides or esters leads exclusively to exo-products.[15,16] This is what would be expected for a kinetically controlled process through B, which should produce the exo or axial C derivative, although this position is less favourable thermodynamically.

In various other instances, however, the skeletal rearrangement A → C does not occur.[8] Thus, the brosylate of A on solvolysis yields the carbinol of A; addition of HCl to bicyclo[2,2,2]octene-2 leads to the chloride of A. Further, 2-aminobicyclo-[2,2,2]octane and nitrous acid give the non-rearranged carbinol. As in the case of bicyclo[2,2,1]heptene-2, free-radical additions at the double bond in bicyclo[2,2,2]-octene-2 give non-rearranged products. Halogenation of bicyclo[2,2,1]heptane[1] as well as of bicyclo[2,2,2]octane also produces type A products.

On the basis of many of the above data, Walborsky supposed that the ion A would rearrange only when its lifetime was sufficiently long,[8] step A → B being relatively slow.

Doubt as regards this plausible hypothesis arises from the fact that the opposite rearrangement has been observed, bicyclo[3,2,1]octene-2 reacting with acetic acid containing some sulphuric acid to produce mainly the acetate of A.[12] In our opinion this means that B reacts preferentially and irreversibly with acetate ion or acetic acid in such a fashion that the thermodynamically unfavourable [2,2,2]-acetate is formed. Therefore, failure to rearrange in reactions of type A derivatives may be due at least in part to kinetic control involving a reaction of the intermediate B and need not be attributable exclusively to the slowness of the step A → B as assumed by Walborsky. Apparently, this point requires further experimentation.

2. *Halogenations of bicyclo*[2,2,2]*octane*

The higher reactivity of tertiary hydrogens compared with secondary ones contrasts with the very low reactivity of the bridgehead positions in bicyclo[2,2,1]heptane. Apparently, the bicyclo-octane molecule is sufficiently flexible to permit the near-planar configuration at the bridgehead required for a favourable transition state. The bridgehead bromide, however, is reported to be about $10^5\times$ less reactive in solvolysis than t-butylbromide, though much more reactive than 1-bromobicyclo-[2,2,1]heptane.[17] This would indicate that the transition state in a solvolysis reaction has a greater sensitivity as regards deviations from "planarity" than that in a hydrogen abstraction by atomic chlorine. In the latter reactions only little bond-breaking may

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* In a paper on "*cis*- and *trans*-bicyclo[3,2,1]octanol-2" by A. A. Youssef, M. E. Baum and H. M. Walborsky, the preference for the equatorial form of the alcohol is demonstrated experimentally, the equatorial/axial ratio being about 1g at equilibrium.

[15] J. D. Roberts, W. Bennett and R. Armstrong, *J. Amer. Chem. Soc.* **72**, 3329 (1950).

[16] S. Winstein and D. Trifan, *J. Amer. Chem. Soc.* **74**, 1147 (1952).

[17] W. von E. Doering, M. Levitz, A. Sayigh, M. Sprecher and W. P. Whelan, Jr., *J. Amer. Chem. Soc.* **75**, 1008 (1953).

be necessary to reach the transition state and this would then be subject to little strain at the bridgehead.[18]

As pointed out in Part I,[1] the activation enthalpy for hydrogen removal from the methylene groups by a chlorine atom is probably lower in bicyclo[2,2,1]heptane than in cyclohexane (cf. Table 2). The same may be true in the case of bicyclo[2,2,2]octane; here, a numerical comparison cannot be made from the data because of the appreciable contributions from the tertiary hydrogens (Table 1). The lower overall reactivity of bicyclo[2,2,2]octane compared with cyclohexane (Table 2) is apparently due to a lower entropy factor, the reason for which is not obvious. It may be noted that the acetolysis rate of bicyclo[2,2,2]octyl-2-brosylate is appreciably greater than that of the cyclohexyl ester;[19] here, the strain should be relieved to a larger extent among other things since the brosylate group is more bulky than a hydrogen atom.

EXPERIMENTAL

1. *Preparation of bicyclo*[3,2,1]*octene*-2 *and bicyclo*[2,2,2]*octene*-2

A 2-litre steel autoclave, containing 103 g cyclohexadiene-1,3 prepared as described by Hine *et al.*[5] was charged with ethylene to a pressure of 50 atm. The reaction vessel was set in rotation and kept at 280° ± 20° for 34 hr. Distillation of the contents yielded 25 g of a liquid with b.p. 133–135°, $n_D^{20} = 1{\cdot}4793$; $d_{19}^{19} = 0{\cdot}8961$. This liquid was dissolved in 30 ml methanol and cooled to $-60°$. The crystals formed were recrystallized from pentane and finally sublimed, m.p. 43–45° (lit[12] 47°).

Ozone absorption indicated the presence of 0·98 double bond per molecule calc. for C_8H_{12}. (Found: C, 88·8; H, 11·4; calc. for C_8H_{12}: C, 88·9; H, 11·1%).

The crystalline material was hydrogenated in ether-acetic acid over a Pt catalyst at atmospheric pressure to yield bicyclo[3,2,1]octane, which after repeated sublimation melted at 136–137·5°. Before sublimation infra-red and mass spectrometry indicated the presence of not more than 3% of bicyclo-[2,2,2]octane and 5–6% of ethylcyclohexane. The pure compounds were used as spectroscopic standards.

When the Diels-Alder reaction described above was carried out in the presence of about 1·0% molar of pyridine the white, solid bicyclo[2,2,2]octene was obtained, boiling at 133–135°, m.p. 98–106°; after sublimation from P_2O_5 the yield was 20% and m.p. 112–113°.

On heating 10 g bicyclo[2,2,2]octene-2 with 1 g moist ferric chloride for 5 hr at 250°, a mixture of 37% of the [2,2,2]- and 63% of the [3,2,1]-isomer was obtained. The analysis of this mixture was carried out with the aid of mass spectrometry after hydrogenation.

2. *Hydration and oxidation of bicyclo*[3,2,1]*octene*-2

The bicyclo[3,2,1]octene-2 crystals m.p. 43–45° were hydrated with diluted sulphuric acid, as described by Newman *et al.*[14] for bicyclo[2,2,2]octene. The reaction product, bicyclo[3,2,1]octanol-2, was sublimed repeatedly, finally from anhydrone. Then its m.p. 187–187·5° and those of its phenylurethane (126°) and *p*-nitrobenzoate (79·5–81°) were in agreement with those mentioned in the literature.[13,14] The melting points were not lowered by admixture with bicyclo[3,2,1]octanol-2 and derivatives, respectively, which were prepared from bicyclo[2,2,2]octene-2 according to Newman *et al.*[14]

The oxidation of bicyclo[3,2,1]octene with potassium permanganate was carried out according to the method used by Birch *et al.*[20] A solution of 2 g of the crystals m.p. 43–45° in 10 ml iso-octane was poured while stirring with a vibrating mixer into a 2-litre beaker containing 150 ml water. A solution of 7·5 g potassium permanganate in 225 ml water was added as fast as decolorization occurred; the temp was held below 50°. To keep the solution neutral, a steady stream of carbon dioxide was passed in. After the end of the reaction, sulphur dioxide was passed in to bring the precipitated manganese dioxide into solution. The solution was acidified with sulphuric acid and exhaustively extracted with

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[18] e.g. G. A. Russell and H. C. Brown, *J. Amer. Chem. Soc.* **77**, 4031 (1955).

[19] Unpublished results by H. M. Walborsky and M. Baum as quoted by A. Streitwieser, *Chem. Rev.* **56**, 571 (1956).

[20] S. F. Birch, J. W. Oldham and E. A. Johnson, *J. Chem. Soc.* 818 (1947).

ether. The ether was dried over sodium sulphate. After evaporation of the ether, a solid residue remained with m.p. 118–130° (2·2 g). Crystallization from benzene yielded 1·8 g (60%) white crystals m.p. 138–139° (lit 139°[12]).

Titration indicated an equivalent weight of 86; calculated for $C_8H_{12}O_4$: 86.

A solution of 1·7 g of the C_8 dicarboxylic acid and 2 g CrO_3 in 100 ml acetic acid was heated on the steam bath for 3 hr; the solution became green. The acetic acid was removed in vacuo and the solid residue was extracted with ether and recrystallised from benzene. Its m.p., 117–119°, was not depressed on admixture with a pure sample of *cis*-1,3-cyclopentanedicarboxylic acid m.p. 118–119°, obtained by oxidation of norbornene.

3. *Chlorination of bicyclo*[2,2,2]*octane*

5·5 g bicyclo[2,2,2]octane (50 mmoles) was dissolved in 30 ml carbon tetrachloride and brought to 28°. 17 ml 1·805 N Cl_2 in CCl_4 (15 mmoles) was added and the mixture was irradiated with ultra-violet light. After 2 min it was decolorized and the temp had risen to 33°.

The carbon tetrachloride was removed under reduced pressure and a solid residue of 5·1 g remained. This residue was analyzed by infra-red and mass-spectrometrical methods.

4. *Competitive halogenations of bicyclo*[2,2,2]*octane and cyclohexane*

An example is given of the competitive chlorination of the above cyclanes. A solution of 1·376 g (12·5 mmoles) bicyclo[2,2,2]octane and 1·049 g (12·5 mmoles) cyclohexane in 30 ml carbon tetrachloride was cooled to 5° and 6 ml of a 0·98 N solution of chlorine in carbon tetrachloride was added under ultra-violet irradiation; the temp was kept at 5°. When the reaction was finished, the carbon tetrachloride was distilled under reduced pressure in an eight-plate column until the residue had a volume of about 5 ml. This residue was analysed by gas-liquid chromatography, using a column of dinitrodiphenic acid C_5–C_6 ester on sterchamol at 140°, with β-ray detection. Hydrogen was used as the carrier gas.

The integrated peaks for the bicyclo-octyl chloride and cyclohexyl chloride were 297 and 238, respectively.

The relative molar quantities were 279/144·5 = 1·93 and 238/118·5 = 2·01; in other words, the mixture of chlorides contained 49% bicyclo[2,2,2]octyl chloride and 51% cyclohexyl chloride, hence

$$\frac{K_c}{K_b} = \frac{\log\left(1 - \frac{0{\cdot}51 \times 2{\cdot}94}{12{\cdot}5}\right)}{\log\left(1 - \frac{0{\cdot}49 \times 2{\cdot}94}{12{\cdot}5}\right)} = 1{\cdot}04.$$

Bromation experiments were carried out analogously.