[Contribution from the Department of Chemistry, Duke University]

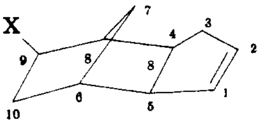
Reactions of 9-Halodihydro- and -tetrahydro-*exo*-dicyclopentadienes with Strong Bases[1]

GEORGE T. YOUNGBLOOD[2] and PELHAM WILDER, jr.[3]

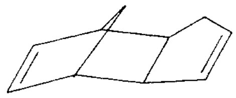
Received June 20, 1956

The reactivity of three 9-halo-9,10-dihydro-*exo*-dicyclopentadienes (I, II, III) and two new 9-halotetrahydro-*exo*-dicyclopentadienes (VI, VII) toward strong bases (alcoholic potassium hydroxide and sodium amide in ether) has been investigated. Elimination was found to occur to some extent in every case, but displacement occurred only in the reaction of the iodide (III) with alcoholic potash. These results are discussed in terms of the factors which influence relative yields of elimination and displacement products.

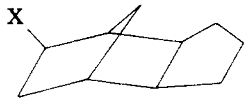
The preparation of 9-chloro-(I), 9-bromo- (II), and 9-iodo-9,10-dihydro-*exo*-dicyclopentadiene[4,5] (III) and other derivatives of dicyclopentadiene[6] was first reported by Bruson and Riener who observed that the 9-chloro-compound (I) was remarkably inert toward hydrolysis and displacement reactions and suggested that a *neo*-pentyl structure was responsible. In their studies concerning the nature of the rearrangement in this series, Bartlett and Schneider clearly showed that these compounds were members of the little known *exo*-dicyclopentadiene series and suggested that the inertness of the halogen was the result of the effective shielding from rearward attack[7] by the bicyclo[2.2.1]heptyl ring itself. In a subsequent communication Bartlett and Goldstein reported that treatment of the 9-iodo-compound (III) with alcoholic potash gave two products, dicyclopentenyl alcohol (IV) and the new *exo*-dicyclopentadiene[8] (V). The present investigation was initiated to study the chemical reactivities of the three unsaturated halides above (I, II, III) and of two new saturated halides 9-chloro- (VI) and 9-bromo-tetrahydro-*exo*-dicyclopentadiene (VII) toward strong bases (alcoholic potassium hydroxide and sodium amide in ether) and to interpret these results in terms of the factors which influence relative yields of elimination and substitution products. The results of this investigation are recorded in Table I. The two new saturated halides (VI and VII) were prepared in excellent yield by hydrogenation of the corresponding unsaturated halides over Adams' oxide in ethyl acetate solution.



I. X = Cl; II. X = Br;
III. X = I; IV. X = OH.



V



VI. X = Cl
VII. X = Br
VIII. X = OH

DISCUSSION

Although the dicyclopentyl halides are secondary halides which are generally subject to displacement and elimination reactions, it should be remembered that these halides contain certain steric features which make them unique. The bicyclo[2.2.1]heptyl system imposes certain steric conditions which make it virtually impossible for a displacing group to approach directly the rearward (*endo*) side of the carbon atom with the halogen. This structural enigma is pointed out by the dearth of conventional S_N2 displacements in this series. Even with phenoxide ion, a good nucelophilic reagent, no ether was obtained from bromide II; in fact, Cristol and Brindell have recently reported what is perhaps the first direct displacement in this system.[9] While the direct displacement is sterically retarded, *exo*-norbornyl and isobornyl chlorides are not particularly inert under solvolytic conditions.[10,11] In these instances

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[1] (a) For previous paper in this series, see Wilder and Youngblood, *J. Am. Chem. Soc.*, **78**, 3795 (1956). (b) Taken in part from a thesis submitted by G. T. Youngblood to the Graduate School of Duke University in partial fulfillment of the requirements for the M.A. degree, October 1955.

[2] American Cyanamid Pre-doctoral Fellow, 1955–1956.

[3] Author to whom inquiries should be directed.

[4] Previously referred to as halo-dihydro-*nor*-dicyclopentadienes, Bruson and Riener, *J. Am. Chem. Soc.*, **67**, 1178 (1945).

[5] The system of numbering used here is that of Alder and Stein [*Ann.*, **496**, 204 (1932)].

[6] Bruson and Riener, *J. Am. Chem. Soc.*, **68**, 8 (1946).

[7] Bartlett and Schneider, *J. Am. Chem. Soc.*, **68**, 6 (1946).

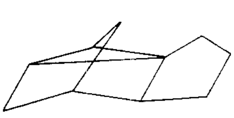
[8] Bartlett and Goldstein, *J. Am. Chem. Soc.*, **69**, 2553 (1947).

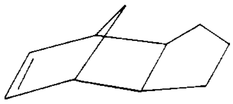
[9] Cristol and Brindell, *J. Am. Chem. Soc.*, **76**, 5699 (1954).

[10] Roberts, Bennett, and Armstrong, *J. Am. Chem. Soc.*, **72**, 3329 (1950).

[11] Winstein, Morse, Grunwald, Jones, Corse, Trifan, and Marshall, *J. Am. Chem. Soc.*, **74**, 1127 (1952).

anchimeric assistance[12,13] with displacement gives rise to a mesomeric cation, the so-called non-classical carbonium ion,[11,12,14] which in turn undergoes reaction. Another type of indirect displacement occurs when a norbornyl halide is treated with alkali to produce a nortricyclenic derivative.[15,16,17] In the dicyclopentadienyl chlorides and bromides, participation of the neighboring group at carbon atom C.4 seems to be sterically hindered by the strain imparted to the *cis*-cyclopentane ring at C.4 and C.5. It is significant that in none of the reactions of these halides with base did a nortricyclenic derivative (IX) eventuate


IX


X

This steric inhibition of anchimeric participation perhaps contributes to the stability of the bromides and chlorides. This picture, however, is complicated by the fact that the iodide (III) yields both olefin and some alcohol[8] and that the alcohol has the same stereochemical configurations as the original iodide (III). It seems remarkable in the transition from bromine to iodine that a significant difference in the relative yields of elimination and displacement products should result.

The reluctance of the chlorides (I and VI) and bromide (VII) to undergo elimination in the presence of amide ion is unusual. Hughes has pointed out that, for elimination reactions, there is usually no appreciable steric factor involved in the approach to hydrogen by the reagent.[18] In one experiment with phenoxide ion in aqueous alcohol the yield of olefin was of the same magnitude as that produced by amide ion. The differences in the yields of olefin in absolute ethanol and 95% ethanol are real, but are differences of degree rather than of kind. In one experiment with the saturated bromide (VII) and potassium hydroxide in 50% (by volume) ethanol only an inferior yield of olefin, relative to the yield in absolute or 95% ethanol, was realized.

From Table I it is apparent that the unsaturation in compounds I, II, and III plays little, if any, part in the reactivity of the halides with base. This observation is consistent with the stereochemistry of the *exo*-configuration of the halides in which the unsaturation is essentially insulated by the *endo*-methylene group from the seat of reaction.

No mention has been made thus far of the olefin 1,2-dihydro-*exo*-dicyclopentadiene (X) which resulted from the alkali treatment of the saturated chloride (VI) or bromide (VII). Bruson and Riener

TABLE I

REACTION OF HALO DICYCLOPENTADIENES WITH STRONG BASES

Halide	Base	Solvent	Elimination, %	Displacement, %	Recovery, %	Reaction time, (hrs.)	Base, moles	Halide, moles	Solvent, ml.	Ref.[a]
I	KOH	abs. EtOH	14	0	70	24	0.4	0.1	200	
	KOH	95% EtOH	55	0	27	24	0.8	0.2	400	
	KOH	95% EtOH	0	0	—	24	—	—	—	7
	$NaNH_2$	NH_3 and $(C_2H_5)_2O$	3	0	83	16	0.2	0.1	500 NH_3 200 Et_2O	
VI	KOH	abs. EtOH	22	0	64	24	0.6	0.15	300	
	$NaNH_2$	NH_3 and $(C_2H_5)_2O$	0	0	83	6	0.2	0.12	500 NH_3 200 Et_2O	
II	KOH	abs. EtOH	67	0	12	24	0.8	0.2	400	
	KOH	95% EtOH	77	0	0	24	0.8	0.2	400	
	KOH	95% EtOH	16	0	60	24	1.0	0.23	500	
VII	KOH	abs. EtOH	78	0	12	24	0.8	0.18	400	
	KOH	95% EtOH	77	0	7	24	2.0	0.47	800	
	KOH	50% H_2O 50% EtOH	34	0	57	24	4.0	0.92	400 H_2O 400 EtOH	
	$NaNH_2$	NH_3 and $(C_2H_5)_2O$	7	0	80	4	0.5	0.25	500 NH_3 200 Et_2O	
III	KOH	abs. EtOH	81	0	0	24	0.8	0.2	400	
	KOH	95% EtOH	68	20	0	48	0.88	0.27	400	
	KOH_2	95% EtOH	59	30	—	24	0.88	0.36	—	8
	$NaNH_2$	NH_3 $(C_2H_5)_2O$	57	0	21	18	0.5	0.4	500 NH_3 200 Et_2O	

[a] Where no reference is indicated, the source is the present investigation.

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(12) Winstein and Holness, *J. Am. Chem. Soc.*, **77**, 3054 (1955).

(13) Winstein, Lindegren, Marshall, and Ingraham, *J. Am. Chem. Soc.*, **75**, 147 (1953).

(14) Kwart, *J. Am. Chem. Soc.* **75**, 5942 (1953).

(15) Ver Nooy and Rondestve lt, *J. Am. Chem. Soc.*, **77**, 3583 (1955).

(16) Winston and Wilder, *J. Am. Chem. Soc.*, **76**, 3045 (1954).

(17) Alder and Brochhogen, *Ber.*, **87**, 167 (1954).

(18) Hughes, *Quart. Revs.*, **5**, 263 (1951). See also H. C. Brown, *J. Chem. Soc.*, 1264 (1956).

have reported the preparation of this compound by the dehydration with phosphoric acid of 9-hydroxy - tetrahydro - *exo* - dicyclopentadiene[19] (VIII), but the olefin reported by Bruson and Riener is not the same one obtained in this work. The new olefin prepared in this investigation readily gave a derivative with phenyl azide and was oxidized by permanganate to a dicarboxylic acid, $C_{10}H_{14}O_4$, m.p. 175–176°. The olefin of Bruson and Riener gave no derivative with phenyl azide and on oxidation with permanganate gave a dicarboxylic acid,[1a] $C_{10}H_{14}O_4$, m.p. 161–163°. An intimate mixture of the two acids melted at 129–133°.

EXPERIMENTAL[20]

9-Chloro-9,10-dihydro-exo-dicyclopentadiene (I) was prepared by the method of Bruson and Riener,[4] b.p. 80–83° (1.5 mm.) [reported 102–104° (10–12 mm.)].

9-Bromo-9,10-dihydro-exo-dicyclopentadiene (II) was prepared by the method of Bruson and Riener,[4] b.p. 112–115° (12 mm.) [reported 113–114° (11 mm.)].

9-Iodo-9,10-dihydro-exo-dicyclopentadiene (III) was prepared by the method of Bruson and Riener,[4] b.p. 130–133° (12 mm.) [reported 130–132° (11 mm.)].

9-Chlorotetrahydro-exo-dicyclopentadiene (VI) was obtained by the catalytic hydrogenation of the corresponding unsaturated halide (I). A solution of 56.3 g. (0.33 mole) of I in 50 ml. of ethyl acetate was treated for 12 hours with hydrogen at an average pressure of 50 p.s.i. over a platinum oxide catalyst. The catalyst then was removed by filtration and the solvent in turn was removed by evaporation under diminished pressure. Distillation of the oily residue gave 53.7 g. (94%) of colorless 9-chlorotetrahydro-*exo*-dicyclopentadiene; b.p. 54–55° (0.5 mm.), 88–90° (4 mm.), 117–118° (20 mm.); n_D^{25} 1.5098; d_4^{20} 1.076.

Anal.[21] Calc'd for $C_{10}H_{15}Cl$: Cl, 20.77. Found: Cl, 20.31.

9-Bromotetrahydro-exo-dicyclopentadiene (VII) was obtained by the method described above for the corresponding 9-chloro-derivative (VI). From 106 g. (0.49 mole) of the unsaturated bromide (II) was obtained 100 g. (95%) of 9-bromotetrahydro-*exo*-dicyclopentadiene, a colorless oil, b.p. 79° (0.5 mm.), n_D^{25} 1.5359, d_4^{20} 1.308.

Anal.[21] Calc'd for $C_{10}H_{15}Br$: Br, 37.1. Found: 37.9, 36.5.

Reaction of halides with alcoholic potassium hydroxide. The reaction mixtures were prepared in the proportions and solvents reported in Table I and were heated under reflux for the indicated periods of time. Most of the ethanol then was removed under reduced pressure and the residues were taken up in ether. The ether layers were thoroughly washed with water and dried over $MgSO_4$. After the removal of ether the products were isolated by distillation. The results are recorded in Table I.

The unsaturated chloride (I) and bromide (II) yielded only *exo*-dicyclopentadiene (V), b.p. 80–82° (40 mm.), (reported 51–53° (12 mm.) by Bartlett and Goldstein[8]), while the unsaturated iodide (III) gave dicyclopentenyl alcohol (IV) and olefin. The alcohol, b.p. 124–126° (10–12 mm.) was identified by its *p*-nitrobenzoate, m.p. 129–130° (reported[22] 130–131°).

The saturated chloride (VI) and bromide (VII) gave a new olefin, 1,2-dihydro-*exo*-dicyclopentadiene (X), b.p. 83° (39 mm.); n_D^{25} 1.4930; d_4^{20} 0.9359.

Anal.[23] Calc'd for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found: C, 89.30; H, 10.73.

A mixture of 6.0 g. of olefin X and 5.0 g. of phenyl azide after 12 hours at room temperature gave, after two recrystallizations from absolute ethanol, 6.1 g. (55%) of a pale yellow derivative, m.p. 140–140.5° (reported[24] 142°).

Permanganate oxidation of olefin X. To a solution of 14.5 g. (0.108 mole) of olefin in 200 ml. of acetone was added with stirring 43 g. of potassium permanganate in one-gram portions; the time of addition was two hours. The mixture was stirred mechanically for 24 hours. Water (100 ml.) then was added and the mixture was allowed to stand for 5 more hours. After removal of the MnO_2 by filtration, the solution was acidified with 6*M* hydrochloric acid solution and was extracted five times with ether. The ethereal solution was dried over $MgSO_4$ and then was evaporated almost to dryness. The thick syrup which resulted was crystallized from nitroethane and recrystallized finally from water; the yield of colorless solid was 3.2 g. (15%), m.p. 175–176° (mixture m.p. with an authentic sample[22] 176–179°).

Upon admixture with a sample of the dibasic acid, m.p. 161–163°, obtained by the permangante oxidation of Bruson and Riener's olefin prepared by the dehydration of the saturated alcohol (VIII), a marked depression was observed, mixture m.p. 129–133°.

Reaction of halides with sodium amide. Sodium amide was prepared by dissolving the theoretical amount of sodium in the volume of liquid ammonia recorded in Table I and then by the addition of several crystals of the catalyst $Fe(NO_3)_3 \cdot 9H_2O$. When the blue color indicative of elemental sodium had disappeared the halide in ether solution was added drop wise. As ammonia was lost by evaporation, it was replaced by anhydrous ether. Excess amide ion was destroyed at the end of the reaction by the addition of excess NH_4Cl. The ether solution was washed with water and dried over $MgSO_4$. After the removal of ether, distillation of the residue under reduced pressure yielded the products recorded in Table I. From the unsaturated halides, only *exo*-dicyclopentadiene (V) was obtained; from the saturated halides, 1,2-dihydro-*exo*-dicyclopentadiene (X) was isolated.

Acknowledgment. The authors are indebted to the Duke University Research Council for a grant to one of them (G.T.Y.) during the course of this research.

DURHAM, NORTH CAROLINA

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(19) Bruson and Riener, *J. Am. Chem. Soc.*, **70**, 2809 (1948).

(20) Boiling points and melting points are uncorrected.

(21) Analysis carried out in this Laboratory by the method of Kimball and Tufts [*Ind. Eng. Chem., Anal Ed.*, **10**, 530 (1938)].

(22) Bruson and Riener, *J. Am. Chem. Soc.*, **67**, 723 (1945).

(23) Microanalysis by Galbraith Laboratories, Knoxville, Tennessee.

(24) Alder and Stein, *Ann.*, **504**, 240 (1933).