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THE STEREOCHEMISTRY OF BICYCLO[3.2.1]OCTANE—XI[1]

THE ADDITION OF MONOHALOCARBENE TO NORBORNENE

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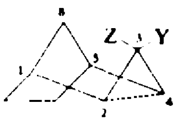
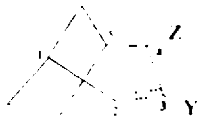
Abstract—Monochloro- and monobromocarbene undergo *exo* addition to norbornene to give *exo-anti*-3-halotricyclo[3.2.1.$0^{2,4}$]octane and *exo*-4-halobicyclo[3.2.1]octene-2. The *exo-anti* adducts were found to be remarkably stable, in contrast to the *exo-syn* adducts, which, though not observed, were presumed to be the labile precursors of the rearranged products. The reasons for these stereochemical differences are discussed.

INTRODUCTION

DIHALOCARBENE reacts with norbornene to form the *exo*-cyclopropane adduct (I) which undergoes facile stereospecific rearrangement to *exo*-3,4-dihalobicyclo[3.2.1]-octene-2 (II).[3,4] It would seem that the rearrangement, which is a special case of the conversion of a cyclopropyl to an allyl halide, involves preferential migration of the *syn-geminal* halogen (Z) rather than the *anti*-halogen (Y) by virtue of accessibility.[5] Apart from these simple steric reasons, the stereochemical result is also in accord with a hypothesis based on molecular orbital considerations.[6] Therefore, it was of particular and crucial interest to prepare and examine *exo*-tricyclo[3.2.1.$0^{2,4}$]-octane derivatives in which only one of the *geminal* substituents at C_3 (Y or Z) could become a leaving group. Accordingly, the present paper is concerned with the



I Z = Y = Cl or Br
III Z = H Y = Cl
IV Z = H Y = Br
XI Z = Cl Y = H
XII Z = Br Y = H



II Z = Y = Cl or Br
VIII Y = H Z = Cl
IX Y = H Z = Br
X Y = H Z = OH

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[1] For Part X see C. W. Jefford, E. Huang Yen and R. T. Medary, *Tetrahedron Letters* No. 51, 6317 (1966).

[2] This paper describes work submitted by R.T.M. in partial fulfilment of the requirements for the M.A. degree at Temple University.

[3] W. R. Moore, W. R. Moser and J. E. LaPrade, *J. Org. Chem.* **28**, 2200 (1963).

[4] C. W. Jefford, S. Mahajan, J. Waslyn and B. Waegell, *J. Am. Chem. Soc.* **87**, 2183 (1965).

[5] The prefixes *syn* and *anti* are applied with reference to the methylene bridge, C_8.

[6] [a] R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.* **87**, 345 (1965); [b] H. C. Longuet-Higgins and E. W. Abrahamson, *Ibid* **87**, 2045 (1965).

stereochemistry of the addition of monohalocarbene to norbornene and of the subsequent rearrangement of the adducts which were obtained.

RESULTS

Monohalocarbene, generated by the interaction of methyllithium and methylene chloride according to the method of Closs,[7] was allowed to react with norbornene. However, the reaction course was found to depend markedly on the provenance of methyllithium. Methyllithium is usually prepared from the reaction of lithium with methyl bromide or methyl chloride. When the former is used, the methyllithium so obtained contains an equimolar amount of lithium bromide as an ether soluble complex. When methyl chloride is used, only a negligible amount of lithium chloride is found complexed with methyllithium.

A. *With* LiMe-LiBr

Reaction resulted in the formation of an oil in an overall yield of about 14% which was found to be a mixture of four products. By preparative VPC two of the products were obtained pure without difficulty. The major product (which had the shorter retention time) had the expected empirical formula $C_8H_{11}Cl$, whereas elemental analysis of the minor product showed it to have the empirical formula $C_8H_{11}Br$. From a consideration of their NMR, IR spectra (see Table 1, Experimental) and chemical evidence their structures were assigned as the *exo-anti*-3-chloro- and 3-bromotricyclo[3.2.1.$0^{2,4}$]octanes (III and IV).

In both cases, the absence of unsaturation, the symmetry indicated by the NMR data and the downfield triplet of intensity 1H, all point unequivocally to an adduct containing cyclopropyl halide. Moreover, the narrowness of the triplet (^3J = 1·5 Hz) exhibited by the cyclopropyl methine proton (on C_3) indicates that the latter is *trans* to the cyclopropyl protons at the ring junction.[8] Only the *exo-anti* (III and IV) and the analogous *endo-syn* structures fit these data. However, the latter structure can be ruled out since reductive dehalogenation of *exo-anti*-3-chloro- and 3-bromo-[3.2.1.$0^{2,4}$]octane gave *exo*-tricyclo[3.2.1.$0^{2,4}$]octane which was identical to an authentic sample.[9]

Further support for the *exo-anti* structures (III and IV) was provided by a consideration of the shielding effect of the cyclopropane ring (and its substituent) on the bridge methylene protons (C_8). In Table 2 the chemical shifts of the methylene (C_8) and bridgehead protons (C_1) of compounds III and IV are assembled with those of *exo*-aziridine V, *exo*-epoxide VI and *exo*-3,3-dichlorotricyclo[3.2.1.$0^{2,4}$]octane VII, all of which have been previously reported.[3,10] The shifts are expressed as differences with reference to those of norbornane.[10] An examination of the data in the Table shows that protons more or less in the plane of the 3-membered ring (H_1) are slightly deshielded to much the same degree (with the exception of V). Protons well above the plane (*anti* C_8) are shielded by a similar amount (0·45 0·68 ppm) despite the

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[7] G. L. Closs and L. E. Closs, *J. Am. Chem. Soc* **82**, 5723 (1963).

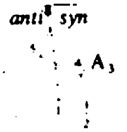
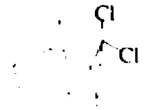
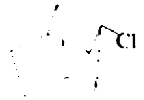
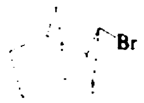
[8] [a] J D Graham and M. T. Rogers, *J. Am. Chem. Soc.* **84**, 2249 (1962); [b] G. L. Closs, R. A. Moss and J. J. Coyle, *Ibid.* **84**, 4985 (1962).

[9] H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc* **81**, 4256 (1959).

[10] K. Tori, K. Aono, K. Kitahonoki, R. Muneyuki, Y. Takano, H. Tanida and T. Tsuji, *Tetrahedron Letters* No. 25, 2921 (1966).

variety of substituents. However, protons *nearly* in the plane (*syn* C_8) still experience shielding, but less appreciably ($\Delta\delta = +0{\cdot}30$ and $+0{\cdot}27$ for III and IV). This slight shielding of the *syn* C_8 proton can be nullified by a vicinal electronegative atom ($\Delta\delta \sim 0$ for V and VI), and be turned into a sizeable deshielding by a contiguous electronegative atom ($\Delta\delta = -0{\cdot}93$) as in VII.[11, 12]

TABLE 2. SHIELDING EFFECTS DUE TO A 3-MEMBERED RING[a]

			Chemical shift differences, Δδ in ppm[b c]		
	Compound		C_8 protons		
			anti	*syn*	H_1
A = NH	V[d]		+0·68	+0·04	−0·09
A = O	VI[d]		+0·63	−0·06	−0·21
	VII[e]		+0·45	−0·93	−0·43
	III		+0·55	+0·30	−0·21
	IV		+0·59	+0·27	−0·23

[a] In CCl_4 solution.

[b] A plus sign indicates shielding.

[c] Compared to the chemical shifts of similar protons in norbornane.

[d] From Ref. 10.

[e] from Ref. 3, also cf. Refs 11, 12.

The two remaining components of the mixture could not be separated by column or VPC as they decomposed in the process. However, their structures were deduced as *exo*-4-chloro- and *exo*-4-bromobicyclo[3.2.1]octene-2 (VIII and IX) by comparison with authentic samples.[13] An indication of the presence of the cyclohexenyl

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[11] R. C. Fort, Jr., G. W. H. Cheeseman and E. C. Taylor, *J. Org. Chem.* **29**, 2440 (1964).

[12] A related example is provided by *exo*-*anti*-8-hydroxybenztricyclo[3.2.1.$0^{2,4}$]octene in which the appropriate cyclopropyl proton on C_3 is strongly deshielded [M. A. Battiste and M. E. Brennan, *Tetrahedron Letters* No. 47, 5857 (1966)]

[13] C. W. Jefford and E. Huang Yen, *Tetrahedron* to appear

grouping was given by the NMR spectrum of the crude mixture of products. Hydrolysis of the mixture with aqueous silver nitrate afforded *exo*-4-hydroxybicyclo-[3.2.1]octene-2 (X) and left the tricyclic compounds III and IV unchanged.

In several different additions the same four products were obtained in much the same yields and proportions. By integration of the signals due to the allylic and cyclopropyl protons, the proportions of compounds III, IV, VIII and IX came out to be 10:5:4:2.

B. *With* LiMe

When methyllithium was prepared from methyl chloride and allowed to interact with methylene chloride in the presence of norbornene, only two products were formed. These were *exo-anti*-3-chlorotricyclo[3.2.1.$0^{2,4}$]octane (III) and *exo*-4-chlorobicyclo[3.2.1]octene-2 (VIII). They were formed habitually in a ratio of 6:1.

DISCUSSION

The formation of both brominated and chlorinated products from methyllithium lithium bromide complex could have occurred by two different reaction courses (i and ii).

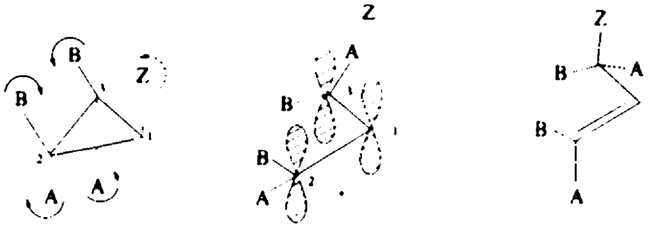
(i) Methyllithium lithium bromide complex and methylene chloride could form both monochloro- and monobromocarbene or their carbenoid precursors, which then add to norbornene: or

(ii) only monochlorocarbene (or its precursor) is generated to give the two chloro products (e.g. III and VIII) which then react further with lithium bromide to give the bromo compounds. However, as *exo-anti*-3-chlorotricyclo[3.2.1.$0^{2,4}$]octane (III) is quite inert under ionizing conditions, course (ii) can be ruled out.

Therefore, both chloro- and bromocarbene are separately generated which then undergo addition exclusively to the *exo* side of norbornene to give the less crowded adducts in the greater amount (*anti* > *syn*). This steric result is in no way incompatible with the general finding that monocyclic and acyclic olefins give rise to the more encumbered adducts predominantly. Closs has suggested that in the latter cases hyperconjugative effects play a determinative rôle in the transition state.[8b] However, such effects are absent in norbornene and therefore, the product composition appears to be determined by steric factors alone.

The remarkable result of such *exo* addition is that *only* the *exo-anti* adducts (III and IV), the major products, were isolated and further, that they were unusually stable. In contrast, no *exo-syn* cyclopropane adducts (XI and XII) were detected under the mild reaction conditions, although addition in the *exo-syn* sense undoubtedly took place. Instead, the products of their rearrangement, *exo*-4-chloro- and 4-bromobicyclo[3.2.1]octene-2 (VIII and IX) were found.

The foregoing results provide an important substantiation of a hypothesis concerning the stereochemistry of the rearrangement of cyclopropyl systems.[6] For a cyclopropyl sulfonate ester or halide (XIII) to ionize, the favored process involves simultaneous rupture of the C_1—Z and C_2—C_3 bonds as depicted in Fig. 1 (solid arrows denote mechanical movement; dashed arrows electronic movement). It can be seen that the cyclopropyl bonds which move apart (C_2 - -A and C_3 - -A) require that the anionoid group (Z) leaves from the side opposite to them. In the *exo*-tricyclo[3.2.1.$0^{2,4}$]octane skeleton (e.g. XI and XII) geometric constraints are such that only the C_1—C_2 and C_4- C_5 bonds can correspond to the C_2- B and C_3- B bonds of the illustration. Therefore rearrangement of the *exo*-tricyclo[3.2.1.$0^{2,4}$]-octane skeleton occurs, in accord with the hypothesis, only when the leaving group at C_3 has the *syn* configuration as in XI and XII, but as not in III or IV.



XIII XIV XV

FIG. 1. Electrocyclic conversion of a cyclopropyl to an allyl system.

Recently,[14, 15] the solvolytic reactivity of several cyclopropyl systems has been similarly interpreted and evidence indicates that, in the solvolytic step, the structure of the intermediate cation has progressed a long way towards that of the allylic cation (XIV). It is important to point out that the present cyclopropyl system, *exo*-tricyclo[3.2.1.$0^{2,4}$]octane, undergoes rearrangement in a *non-SN*1 process in which the anionoid atom Z migrates stereospecifically to the *exo*-C_4 position of the new bicyclo[3.2.1]octene-2 skeleton (e.g. XI → VIII).

Further, although the stereochemistry of both reactant and product have been demonstrated and shown to fit the Hoffmann Woodward hypothesis, an additonal question concerning the nature of the rearrangement process arises; that is the question of whether the rearrangement is a fully concerted process with or without charge separation (XIII → XIV → XV or XIII → XV).

EXPERIMENTAL

Reagents. MeLi in ethereal soln as supplied by Alpha Inorganics contained an equimolar amount of the LiBr and was essentially "unadulterated" when supplied by the Foote Mineral Co.

Spectral determinations. NMR spectra were recorded at 60 MHz on a model A-60 spectrometer (Varian Associates, Palo Alto, Calif) at a temp of about 37° Compounds and mixtures were investigated as Cl_4 solns (ca. 10% wt to vol) containing TMS as a standard. Chemical shifts and coupling constants are estimated to be accurate to ± 1·0 and ±0·1 Hz respectively.

IR spectra were recorded on a Beckmann IR-9 spectrometer.

VPC was carried out on an F and M Laboratory Model 700 analytical chromatograph and on the Nester Faust Prepkromatic preparative chromatograph. Aluminum columns (¼ in. diam. and 2 and 4 m long packed with 25% cyano-silicone 1150 supported on chromosorb W were used at oven temp of 135 145° with He as the carrier gas

A *Reaction of norbornene, using MeLi LiBr*

A soln of MeLi LiBr in ethyl ether (200 ml of a 1·25M soln) was added dropwise to a stirred soln of norbornene (30 g, 0·32M) in CH_2Cl_2 (16 ml, 0·25M) and ether (40 ml). The addition was repeated several times and the crude mixture was then treated in one of three ways.

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[14] C. H. DePuy, L. G. Schnack, J. W. Hausser and W. Wiedmann, *J. Am. Chem. Soc* **87**, 4006 (1965).

[15] P. v R. Schleyer, G. W. van Dine, U. Schöllkopf and J. Paust, *J. Am. Chem. Soc* **88**, 2869 (1966) and Refs cited therein

(i) Excess norbornene and solvent were removed by distillation. VPC of the crude oil showed four components as products, each of which exhibited characteristic signals in the NMR spectrum. The doublet of doublets at 6·02 ppm ($^{3}J_{\text{large}}$ − 10·0 Hz, $^{3}J_{\text{medium}}$ = 6·5 Hz) and the doublet of doubled doublets centred at 5·50 ppm ($^{3}J_{\text{large}}$ = 10·0 Hz, $^{3}J_{\text{medium}}$ = 4·0 Hz, and J_{small} = 1·5 Hz) are due to the vinyl protons of *exo*-4-chloro- and 4-bromobicyclo[3.2.1]octene-2 (VIII and IX). The broad triplets (both 6·5 Hz wide at mid-height ($^{3}J_{\text{large}}$ = 4·0 Hz and $^{3}J_{\text{small}}$ = 2·5 Hz) at 4·21 and 4·50 ppm are due to the allylic protons (VIII and IX). The narrow triplets (3·0 Hz wide) at 2·84 and 2·75 ppm are the cyclopropyl proton (C_3) resonances of *exo*-3-chloro- and 3-bromotricyclo-[3.2.1.0^{2,4}]octane (III and IV). The product compositions resulting from several different addition experiments were estimated from the relative intensities of these signals. A typical ratio is 10:5:4:2 for III, IV, VIII and IX. Yields of crude oil were between 2·8 and 5·2 g which corresponds to a yield of between 7 and 14% based on CH_2Cl_2.

(ii) The crude mixture was poured over its own volume of crushed ice. On work-up 5·2 g of an oil (b.p. 60–70° at 5·6 mm) was distilled and collected. The VPC and NMR spectrum indicated the presence of the same components as described in (i) together with some X. The quantity of X was variable as it came from partial hydrolysis of VIII and IX. By preparative VPC followed by micro-distillation, III and IV were separated and obtained pure. Their spectral data are listed in Table 2 (Found: C, 67·68; H, 7·96; Cl, 23·92. $C_8H_{11}Cl$ (III) Requires: C, 67·37; H, 7·72; Cl, 24·91%. Found: C, 51·73; H, 5·92; Br, 42·87. $C_8H_{11}Br$ (IV) requires: C, 51·36; H, 5·92; Br, 42·75%.) It proved repeatedly impossible to obtain better agreement between the calculated and found halogen percentages.

Table 1. NMR and IR spectral data of *exo-anti*-3-chloro- and 3-bromotricyclo[3.2.1.0^{2,4}]octane (III and IV)

III (Major)	IV (Minor)	Intensity	Assignment
T at 2·84 ppm (^{3}J ~ 1·5 Hz)	T at 2·75 ppm (^{3}J ~ 1·5 Hz)	1H	C_3
S at 2·41 ppm	S at 2·43 ppm	2H	C_1, C_5
S at 1·36 ppm	S at 1·36 ppm	4H	C_6, C_7
S at 1·08 ppm	S at 1·17 ppm	2H	C_2, C_4
D at 0·91 ppm (^{2}J ~ 10·5 Hz)	D at 0·94 ppm (^{2}J ~ 10·5 Hz)	1H	C_8
D at 0·66 ppm (^{2}J ~ 10·5 Hz)	D at 0·62 ppm (^{2}J ~ 10·5 Hz)	1H	C_8
Max at 782 cm^{-1} (C-Cl stretching)	Max at 722 cm^{-1} (C-Br stretching)		

T = Triplet, S = Singlet, D = Doublet.

(iii) To a soln of the crude oil, (obtained after aqueous work-up; 3·2 g) in acetone (15 ml), was added a soln of $AgNO_3$ (4·0 g) in water (15 ml). The mixture was gently boiled; afterwards, silver halide was removed by filtration. The aqueous acetone soln on work-up afforded 3·0 g of product. Column chromatography (on 1 g of product) over neutral alumina (50 g) gave a mixture of III and IV on elution with pentane. Elution with ether afforded X (150 mg, m.p. 66–70°) identical to an authentic sample.[16]

B. *Reaction of norbornene using* MeLi

The same procedure and amounts were used as before (A). Excess MeLi was decomposed by pouring the reaction mixture over crushed ice. After work-up and distillation (2·5 g, 7·0%), VPC and NMR indicated a mixture containing X, VIII and III in the ratios of 1:2:12.

Stability of exo-anti-3-*chloro and* 3-*bromotricyclo*[3.2.1.0^{2,4}]*octane* (III *and* IV). Under the above experimental conditions; *viz.* temps of 140° for short periods of time (10 min) and in the presence of Ag

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[16] We thank Professor H. L. Goering for kindly sending a sample of *exo*-4-hydroxybicyclo[3.2.1]octene-2 for comparison.

cation, both III and IV were stable. As an additional test of thermal stability, III was heated in a sealed tube at 188 194° for 16 hr. No decomposition was found to have occurred.

Reductive dehalogenation of exo-anti-3-*chloro- and* 3-*bromotricyclo*-[3.2.1.$0^{2,4}$]*octane* (III *and* IV). A soln of compds III and IV (2·0 g, 60% and 40% respectively) in ether (20 ml) was added dropwise under a N_2 atm to a stirred soln of Na (6·2 g) in liquid ammonia (50-70 ml) in a flask cooled by a solid CO_2-acetone bath. After addition, excess ammonia was allowed to evaporate while ether (100 ml) was added simultaneously. MeOH (10 ml) in ether (100 ml) was added to decompose excess Na and sodamide, followed by more MeOH and water to complete the decomposition. On work-up an oil (1·3 g) was obtained which was identical to *exo*-tricyclo[3.2.1.$0^{2,4}$]octane.[9]

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