Stereochemistry and Mechanisms of the Addition of Deuterium Chloride to Bicyclo[2.2.1]heptadiene (Norbornadiene) and to Tetracyclo[3.2.0.$0^{2,7}$.$0^{4,6}$]heptane (Quadricyclene)

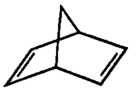
TERENCE C. MORRILL* AND BRIAN E. GREENWALD

Department of Chemistry, Rochester Institute of Technology, Rochester, New York 14623

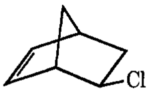
Received January 7, 1971

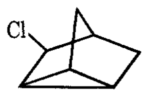
Addition of hydrogen chloride and deuterium chloride to bicyclo[2.2.1]heptadiene (I, norbornadiene) results in (unlabeled and labeled, respectively) *exo*-dehydronorbornyl chloride (III) and nortricyclyl chloride (IV). The ratio of III/IV varies from 75–85%/25–15% depending upon the solvent and addendum. Labeled III is composed of 57% (±1%) *exo-cis*-3-deuterio-2-dehydronorbornyl chloride (IIIa) and 43% *syn*-7-deuterio-2-*exo*-dehydronorbornyl chloride (IIIb). Addition of deuterium chloride and hydrogen chloride to tetracyclo-[3.2.0.$0^{2,7}$.$0^{4,6}$]heptane (II, quadricyclene) gave (respectively, labeled and unlabeled) III and IV in ratios of 80–87% III/20–13% IV. Labeled III (from II) was composed of 58% (±1%) IIIa and 42% IIIb. The mechanism(s) of addition to I and II must be very similar and neither addition can involve a symmetrically bridged cation as the sole precursor to III. Ionic cleavage of the cyclopropane rings of II are by the inversion process only.

A study of the addition of each of hydrogen chloride and deuterium chloride to each of bicyclo[2.2.1]heptadiene (I, norbornadiene) and its photoisomer tetracyclo[3.2.0.$0^{2,7}$.$0^{4,6}$]heptane (II, quadricyclene)[1] allows a detailed examination of a unique addition to diene I and a similarly detailed examination of the cyclopropane ring cleavage of II.


I


II

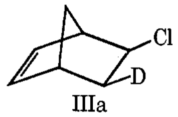

III


IV

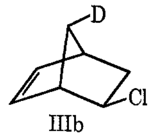
The addition of hydrogen chloride to norbornadiene, which results in *ca.* 80% *exo*-2-dehydronorbornyl chloride (III) and 20% nortricyclyl chloride (IV) (Table I), is unusual since the additions of most ionic addenda result in a majority of nortricyclene derivatives.[2] Exceptions to this nortricyclene isomer predominance are known.[7] The addition of hydrohalic acids to diene I consistently results in the predominance of norbornenyl skeleton adducts.[3,10] Since the incipient norbornenyl cation is known to be prone to homoallylic rearrangement,[5,11] the lack of rearrangement in the case of hydrogen halide addition is worthy of closer scrutiny. Wagner–Meerwein rearrangement often accompanies cationic rearrangements in this system,[3,4,12] and this is detectable by a combination of proton magnetic resonance (pmr) and mass spectroscopic techniques.[4,13]

That the product ratios (III/IV) from the addition reactions reported in Table I are the result of kinetic control is confirmed by the following: equilibration of an 80/20 III/IV mixture with anhydrous ferric chloride in pentane resulted in a 5%/95% (±3) ratio of III/IV; predominance of the nortricyclene derivative in such systems has been found for the corresponding acetates,[4] *p*-bromobenzenesulfonates,[6] and hydrocarbons.[14] Treatment of varying III/IV mixtures with hydrogen chloride (under addition reaction conditions) and with chloride ion was unsuccessful in changing the III/IV ratio.

The portions of the pmr spectra of III (from the addition of hydrogen chloride or deuterium chloride to I) corresponding to the proton on the carbon bearing chlorine[11–15] are shown in Figure 1. This signal, despite its "triplet appearance" in deuteriochloroform (Figure 1a), reveals its multiplicity when examined in a variety of solvents (Figure 1b) and the triplet appearance in some cases is thus a "deceptively simple signal."[16–18] Coupling constants that are pertinent to this signal are listed in Table II ($CDCl_3$). The addition of deuterium chloride to I resulted in labeled III, the pmr spectrum of which (at δ 3.7) is shown in Figure 1d. Past investigations[3,4,6,19a] indicate that Wagner–Meerwein rearrangement may very well lead to *exo-cis*-3-deuterio-2-*exo*-dehydronorbornyl chloride (IIIa) and *syn*-7-deuterio-2-*exo*-dehydronorbornyl chloride (IIIb). The pmr spectrum of III would be expected to be identical with that of unlabeled III (at δ 3.7). The corresponding signal for III would be expected to possess a substan-



IIIa



IIIb

---

[1] W. G. Dauben and R. L. Cargill, *Tetrahedron*, **15**, 197 (1961).

[2] These include the products resulting from the addition to I of bromine,[3] acetic acid with mineral acid catalyst,[3–6] mercuric acetate and methanol,[3] methanol with mineral acid catalyst,[6] and *N*-bromosuccinimide–methanol.[3]

[3] S. Winstein and M. Shatavsky, *Chem. Ind.* (*London*), 56 (1956).

[4] S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *J. Org. Chem.*, **31**, 2719 (1966).

[5] S. J. Cristol, W. K. Seifert, D. W. Johnson, and J. B. Jurale, *J. Amer. Chem. Soc.*, **84**, 3918 (1962).

[6] E. Vogelfanger, Ph.D. Thesis, University of California at Los Angeles, 1963.

[7] These include the adducts of I and each of *p*-toluenesulfenyl chloride,[8] mercuric acetate,[9] and acetic acid with no added catalyst.[4]

[8] S. J. Cristol, R. P. Arganibright, G. D. Brindell, and R. M. Heitz, *J. Amer. Chem. Soc.*, **79**, 6035 (1957).

[9] K. C. Pande and S. Winstein, *Tetrahedron Lett.*, 3393 (1964).

[10] L. Schmerling, J. Luivisi, and R. Welch, *J. Amer. Chem. Soc.*, **78**, 2819 (1956).

[11] J. D. Roberts, *et al.*, *ibid.*, **72**, 3329 (1950); **76**, 4623 (1954).

[12] S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *ibid.*, **88**, 3087 (1966).

[13] S. J. Cristol, R. A. Sanchez, and T. C. Morrill, *J. Org. Chem.*, **31**, 2733 (1966).

[14] P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **80**, 1700 (1958).

[15] J. Paasivirta, *Suom. Kemistilehti B*, **38** (7–8), 130 (1965).

[16] L. M. Jackman and S. Sternhell, "Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Elmsford, N. Y., 1969, p 150.

[17] T. J. Flautt and W. F. Erman, *J. Amer. Chem. Soc.*, **85**, 3212 (1963).

[18] A. F. Thomas, R. A. Schneider, and J. Meinwald, *ibid.*, **89**, 68 (1967).

[19] (a) S. J. Cristol and R. Caple, *J. Org. Chem.*, **31**, 2741 (1966); (b) S. J. Cristol and J. M. Sullivan, *J. Amer. Chem. Soc.*, **93**, 1967 (1971). (c) A referee has criticized ion VI on the basis of ostensibly inappropriate delocalization *via* interaction of orthogonal σ and π systems. Despite this criticism such an ion has been considered in many interpretations of results involving norbornenyl cations.[4–6,11–13,27,28]

TABLE I

ADDITION OF HCl AND DCl TO NORBORNADIENE (I) AND QUADRICYCLENE (II)

Expt	Substrate	Addendum	Solvent/temp	III/IV[a]	IIIa/IIIb[b]	Yield,[c] %
1	I	HCl	CH_2Cl_2/amb[d]	78/22		73
2	I	HCl	Dioxane/amb	80/20		50
3	I	HCl	Ligroin/amb	64/36[e]		5
4	I	DCl	CH_2Cl_2/amb	81/19	57/43	40
5	I	HCl	CH_2Cl_2/−78°	70/30		76
6	I	DCl	CH_2Cl_2/−78°	76/24	57/43	
7	II	HCl	CH_2Cl_2/amb	80/20		
8	II	DCl	CH_2Cl_2/amb	84/16	58/42	
9[f]	II	DCl	CH_2Cl_2/amb	88/12	58/42	

[a] Determined by gas chromatography (glc). [b] Determined by nmr and mass spectroscopy. [c] Determined by glc external standard. [d] Ambient temperature, 20–25°. [e] Roughly consistent with analogous result for pentane/−78° previously reported.[10] [f] Contaminated to the extent of 18% by I.

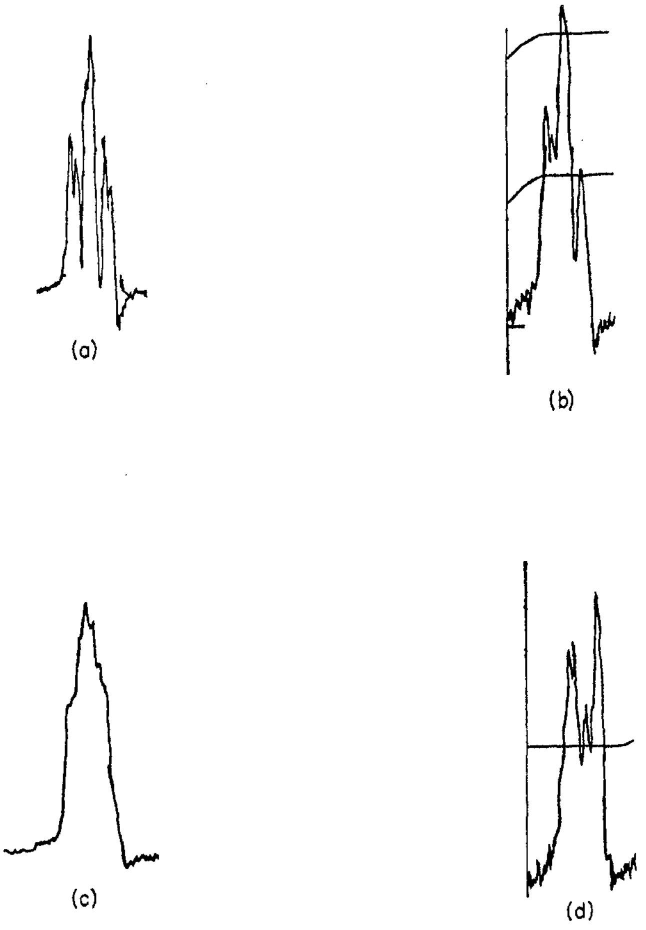


Figure 1.—Pmr spectrum of samples III, δ 3.7 signal, proton on carbon bearing Cl: (a) in $CDCl_3$; (b) in CCl_4; (c) in C_6D_6; (d) labeled in $CDCl_3$.

tially "doublet appearance."[20] The signal at δ 3.7 for labeled III (Figure 1d) is consistent with a sample that is *ca.* 50% IIIa (±10%) and 50% IIIb; the major coupling (J_{2N-3N}, Table II) remains and the spectrum has the appearance of the triplet of IIIb superimposed upon the expected doublet of IIIa. The olefinic protons of unlabeled III absorb at δ 6.05 and the remaining protons absorb at δ 1.4–2.0 with the exception of a *ca.* one-proton signal at δ 2.1. This last signal is assigned to the *syn*-7 proton based on analogy with previous work[19a] and the fact that this signal is

TABLE II

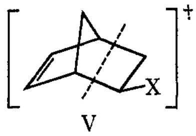
COUPLING CONSTANTS FOR III IN $CDCl_3$[a]

J[b]	Hz	J[b]	Hz
2N-3N	5.4	2N-7A	1.6
2N-3X	4.2	2N-1	1.0

[a] These are in agreement with those previously reported in CCl_4.[15] [b] N = endo, X = exo, A = anti, S = syn.

substantially reduced in labeled III (indicating substantial amounts of IIIb). Thus pmr spectroscopic analysis is consistent with III being a mixture of IIIa and IIIb.

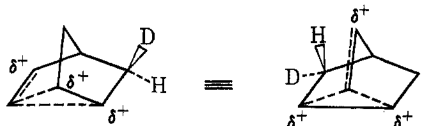
Mass spectroscopic analysis, based on the retro Diels–Alder fragmentation of norbornenyl derivatives (V), has resulted in IIIa/IIIb ratios that are accurate to ±1–2%.[21] That these chlorides undergo such retro



V

Diels–Alder fragmentation pathways has been shown.[21,22] Mass spectroscopic analyses on labeled III (from addition of deuterium chloride to I) indicate that 57% is IIIa and 43% IIIb (reproducibility is well within ±1% limits).

It is thus clear that a symmetrically bridged (disregarding deuterium substitution) cation (VI) cannot be the sole precursor to the formation of labeled olefinic chloride (IIIa and IIIb). Two possible explanations are (a) nonclassical ion VI accompanied by a highly



VI

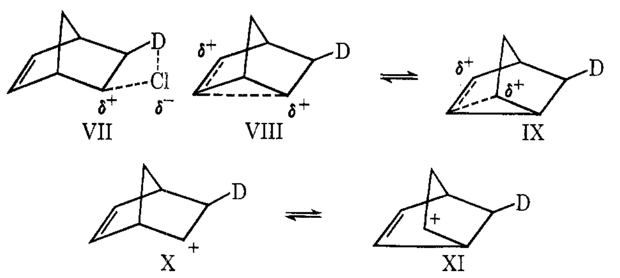
polarized four-centered complex VII and/or (b) equilibrating classical ions VIII and IX (or X and XI) with ion VIII (or X) intercepted somewhat faster than equil-

---

[20] S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *J. Org. Chem.*, **31**, 2726 (1966).

[21] Mass spectroscopic analysis of this type specifically indicates the distribution of deuterium between the C-2,3 and C-1,4,5–7 portions of III (V).[13] However, based on the pmr analysis, mechanism, and other work,[4,6,12,13] this is assumed to be specifically labeled on the C-3 (exo) and C-7 (syn) positions.

[22] W. C. Steele, B. H. Jennings, G. L. Botyos, and G. O. Dudek, *ibid.*, **30**, 2886 (1965).



VII VIII IX

X XI

ibration with ion IX (or XI). Explanation a has been contested[23] on the basis that four-centered reactions (VII) should be subject to 7,7-dimethyl substituent steric control in these systems; this control is not observed.[23,24] Lack of completely symmetrically σ-bridged participation in unsymmetrically substituted norbornene addition reactions has been shown.[23,25] The addition of hydrogen chloride to norbornene-*2,3*-d_2[26] and the addition of deuterium chloride to norbornene[23] both result in a slight preponderance of cis-exo addition (55 and 66%, respectively) as compared to Wagner–Meerwein rearranged product. This is in remarkable coincidence with the results herein in view of the different systems, the intervention (albeit minor) of 6,2 shifts accompanying additions to norbornene[23,24] and possible uncertainties associated with complete reliance on pmr techniques.

Addition of deuterium chloride to benzonorbornadiene results in a 50/50 ratio of Wagner–Meerwein rearranged products (apparently consistent with a single symmetrical cation precursor).[19] However, although the usual[4,13] combination of pmr and mass spectroscopic techniques are used to analyze the products, a somewhat more than desirable uncertainty arises from the loss of hydrogen from the fragment used to measure the Wagner–Meerwein rearranged product.[19] It may be that a few per cent of excess cis-exo addition could escape undetected in that addition reaction.

The addition of deuterium chloride to diene I results in substantial Wagner–Meerwein rearrangement product (III) accompanied by little homoallylic rearrangement product (IV); this is in contrast to labeled acetic acid additions to I where the two types of rearrangement products increase proportionately.[4] In the latter case the relatively weak interaction of an ion-dipole (carbonium ion–acetic acid) allows sufficient mobility for interception of the cation in substantial amounts to form nortricyclyl product.[4–6,11] The tight ion-pair interaction in hydrogen halide addition allows only Wagner–Meerwein rearrangement. The intermediate is likely analogous to intimate ion pairs proposed to account for return products in the solvolysis of 3-deuterio-*exo*-2-dehydronorbornyl-*p*-bromobenzenesulfonate.[12,27,28] If bridging (*e.g.*, ion VI) is not the reason for essentially exclusive exo attack to form III, an argument involving inherent norbornyl steric requirements[22,23] and/or torsional effects[29] may very likely apply. These arguments would have to be adjusted to fit the lack of endo C-5 and C-6 hydrogens in the norbornenyl cation.

It has been shown recently[19b] in the simultaneous additions of deuterium chloride and labeled acetic acid to benzonorbornadiene that the product chlorides show complete Wagner–Meerwein label scrambling and the acetate products form with only partial scrambling. Since chloride ion would be expected to be more nucleophilic than acetic acid, these results would argue against explanation b, above, for "extra" cis-exo addition. This is because ions analogous to VIII and IX (and thus, possibly, VIII and IX) would be expected to lead even more readily to chlorides than acetates with an "extra" cis-exo vicinal label. It was also found that varying the acetic acid, hydrogen (deuterium) chloride, and added chloride ion concentrations over a wide range did not significantly alter the product composition as to chlorides *vs.* acetates or as to Wagner–Meerwein scrambling in either type of product. Thus, if the results involving benzonorbornadiene can be extrapolated to norbornadiene, choice a above might be the preferred over b. The results in this paper do not lead to a clear choice between a and b.[19c]

The additions of deuterium chloride to quadricyclene (II) give results very similar to those obtained in the analogous addition to diene I. Cyclopropane cleavage by ionic reagents has received attention recently as to whether a retention or inversion process accompanies the attack of the electrophile and nucleophile.[30–32] It has been pointed out[31] that nucleophilic attack, with few exceptions, results in cyclopropane ring cleavage with inversion and that electrophilic attack results in inversion and/or retention stereochemistry. The adducts of hydrocarbon II and hydrogen chloride are found to be 84% olefinic chloride (III) and 16% nortricyclyl chloride (IV). Pmr and mass spectroscopic analyses of labeled III (from II addition reactions, carried out as for I) show that 58% (±1%) is IIIa and 42% is IIIb. Thus cis-exo addition again accounts for slightly more than half the olefinic product from II and that the homoallylic rearrangement process is relatively minor (compared to acetic acid additions to I[3–6] and II[6]) as it was for the same reaction for diene I. Using analyses of the major labeled product, III, it is clear that cyclopropane ring cleavage by nucleophile (chloride) occurs essentially completely by inversion (only exo product formed). This is the same as the result of the hydrogen chloride and acetic acid cleavage of nortricyclene (only exo chlorides and acetates formed).[32] Observations of only IIIa and IIIb indicate that electrophilic cleavage of II is also by an inversion process only. This last result is not consistent with the electrophilic cleavage of nortricyclene with deuterioacetic acid[32] or deuterium chloride;[33] in both of these cases electrophilic cleavage involves substan-

---

(23) H. C. Brown and K. T. Liu, *J. Amer. Chem. Soc.*, **89**, 3900 (1967).

(24) H. C. Brown and J. H. Kawakami, *ibid.*, **92**, 201, 202 (1970).

(25) P. v. R. Schleyer, *ibid.*, **89**, 3901 (1967).

(26) J. K. Stille, F. M. Sonnenberg, and T. H. Kinstle, *ibid.*, **88**, 4922 (1966); R. D. Hughes and J. K. Stille, 159th National Meeting of the American Chemical Society, Houston, Tex., 1970, Abstract ORGN 125. Hughes and Stille report that the 1966 report of such addition products are in error due to nmr integration errors. Recent work by these workers shows little 6,2 hydride shift and "excess" cis-exo addition in all hydrogen chloride additions. We are indebted to these workers for release of this information before publication.

(27) J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr., *J. Amer. Chem. Soc.*, **77**, 3034 (1955).

(28) C. C. Lee and B. S. Hahn, *ibid.*, **92**, 2583 (1970).

(29) P. v. R. Schleyer, *ibid.*, **89**, 701 (1967).

(30) S. J. Cristol, J. K. Harrington, Jr., T. C. Morrill and B. E. Greenwald, *J. Org. Chem.*, **36**, 2773 (1971).

(31) S. J. Cristol, W. Y. Lim, and A. R. Dahl, *J. Amer. Chem. Soc.*, **92**, 4013 (1970).

(32) A. Nickon and J. H. Hammons, *ibid*, **86**, 3322 (1964).

(33) J. M. Brown and M. C. McAvor, *Chem. Commun.*, 238 (1969).

tial amounts of both inversion and retention. Molecular model examination indicates no torsional driving forces[29] to exo deuterium attack on II; these forces might be valid for nucleophilic attack on any of cations VIII–XI. In addition there are no C-5,6 endo hydrogens to direct electrophilic or nucleophilic attack.

Because of the large similarity in product compositions arising from I and II, it is important to know the possibilities regarding the interconversion of I and II under the reaction conditions. This is difficult to assess due to the extremely rapid rate of addition to both I and II (>90% reaction after 5 min; see Experimental Section). Also, the reproducibility of the unreacted hydrocarbon composition leaves much to be desired. It does seem clear, however, that the rates of addition to I and II are very similar (see competition reactions, Experimental Section). It also appears, in addition reactions involving II only at the start, that I and II are *both* part of the unreacted hydrocarbons after greater than 90% reaction. Thus, although II seems to convert to I under the reaction conditions, a substantial part (roughly half) of the product chlorides, in additions to II, actually arise from II. The ratio of IIIa/IIIb therefore must be fairly close to 58/42. Control experiments on II using sulfuric acid were even less satisfying; no conversion to I (<5%) was observed, but conversion of II to adduct (ostensibly) was essentially instantaneous.

An intriguing result of this comparative study is that, although results observed for I and II treated with labeled addendum are consistent with the somewhat separate fields of ionic additions to norbornenyl olefins[3–6,8–10,22–25] and ionic cleavage of cyclopropane rings,[30–33] the two sets of results are essentially identical. These indicate that one need not consider the reaction of I and II as requiring separate explanations. Within the limitations of the experiments described herein, the intermediate(s) arising from additions to I and II could be the same. Such similarities are not always the case; additions of various common addenda to I[3–6] and II[1,6,34] often give different product mixtures as to both homoallylic and Wagner–Meerwein rearrangement, and the addition of hydrogen chloride to quadricyclenedicarboxylic acid gives no olefinic product.[30]

Experimental Section

Proton magnetic resonance spectra were determined on a Perkin-Elmer R-20 (60 MHz) instrument. Alkyl chlorides III and IV were prepared as described below (for Table I) and proved identical with those reported earlier.[10,11] Gas chromatographic (glc) analyses were carried out on a Varian 1520B instrument using a 10 ft × 0.25 in. 15% Carbowax 20M column on Chromosorb W. At a column temperature of 175° and a flow rate of 50 cm^3/min, the retention times of III and IV were respectively 6.5 and 8.5 min. Quadricyclene (II) was prepared from diene I by a literature procedure.[1,35] II, however, could not be obtained free of diene I by spinning-band distillation as described.[35] Pure samples of II for analysis and reactions were collected from the instrument and column (used for III and IV analyses) above at a column temperature of 80° and injection and detection block temperatures of 90 and 80°, respectively. Product ratios (III/IV) were determined by peak integration (triangulation) assuming equal molar responses of III and IV. Retention times of I and II (on 80° column) were 12.8 and 23.7 min, respectively, at a flow rate of 50 cm^3/min. Norbornadiene (I) was Eastman and was distilled immediately prior to use.

Table I.—The experiments listed in Table I were carried out by allowing hydrogen chloride (Matheson Coleman and Bell) gas to bubble through (*via* a fritted tube) a solution of I or II in the solvent listed (at room temperature) for 6 hr. The mixture was then stirred overnight (after removing the hydrogen chloride inlet tube). Analytical scale samples (glc) were obtained directly by neutralization of the reaction mixture with sodium carbonate. Preparative scale samples were vacuum distilled.[11] The addition of deuterium chloride was carried out as above using the labeled gas prepared by the method of Dewar and Fahey.[36] Samples of labeled adducts III and IV were worked up as described above. All samples of III and IV for mass spectroscopic and pmr analyses were collected from the gas chromatograph under the conditions listed above.

Equilibration of III/IV Mixtures.—An 80/20 (III/IV) mixture of chlorides was allowed to reflux over anhydrous ferric chloride in pentane for 3–4 days. Repetition of this experiment (three runs) gave III/IV ratios of 5% III/95% (±5%) IV before substantial loss of sample.

Subjection of a III/IV = 83/17 mixture of chlorides to the methylene chloride addition reaction (except for a day longer) of Table I resulted in no change in the III/IV ratio and no substantial loss of sample. A sample of predominately IV when treated with lithium chloride or tetra-*n*-butylammonium chloride in dimethylformamide resulted in no change in the IV/III ratio.

Stability of Quadricyclene (II) to Strong Acid Conditions.—Pure samples (from glc) of II in methylene chloride and carbon tetrachloride were treated in pmr spectrometer tubes with 2 drops of concentrated sulfuric acid. Despite evidence of substantial reaction (darkening of solution, heat evolution), the olefinic peaks of diene I were not detectable immediately or upon periodic pmr analysis over 24 hr. Olefinic peaks (broad, not in the region of I absorption) did appear which were more consistent with a monosubstituted norbornene.

Mass Spectral Analyses.—Conditions for the mass spectroscopic analysis of chloride III have been published.[22] The composition of III in terms of IIIa and IIIb was determined by measuring the intensities of the pertinent peaks and converting these intensities to per cents designating the highest peak in the immediate mass region as 100% and expressing the neighboring peaks in relation to the highest peak. In Table III are given data for labeled III from the addition of deuterium chloride to II at room temperature and a sample calculation is given below. The intensity of the *m/e* 128 peak is taken to be due entirely to unlabeled III, since unlabeled III does not show a significant *m/e* 127 (P − 1) peak and thus singly labeled III would not be expected to result in significant P − 1 (*m/e* 128). The intensity of *m/e* 129 is thus taken to be due to monodeuterated III plus the per cent of *m/e* 128 due to its isotopic contribution to *m/e* 129 (7.7%).[37]

TABLE III

m/e	Raw data (cm)	%
128	0.40	8.5
129	4.72	100.0
130	0.52	11.0
131	1.50	31.8
66	20.1	100.0
67	13.8	68.6

Thus (no. d_1) (or total single deuteration of III) is calculated by no. d_1 = 100% − [8.5(7.7%)] = 99.3; no. d_0 = 8.5.

$$\% \, d_1 = 100\left(\frac{99.3}{99.3 + 8.5}\right) = 92.2\% \text{ labeled III}$$

---

[34] S. J. Cristol and R. A. Sanchez, University of Colorado, unpublished results.

[35] C. D. Smith, Organic Synthesis Submission, May 1969 Circulation, Preprint 1657.

[36] M. J. S. Dewar and R. C. Fahey, *J. Amer. Chem. Soc.*, **85**, 2245, 2248 (1963).

[37] R. Silverstein and G. Bassler, "Spectrometric Identification fo Organic Compounds," Wiley, New York, N. Y., 1967, Chapter 2.

TABLE IV

Expt	% *d* in III	% *d* in C_5 fragment	% IIIb of labeled III
4	83.3	35.9	43.2
6	90.0	38.8	43.2
8	92.2	38.7	42.0
9	85.0	35.6	41.9

TABLE V

II, ml	I, ml	Time of HCl addition, min	Time stirred, min	I, %	II, %	III, %	IV, %
0.50		10	60	4.7	0.6	76.3	18.4
0.50		10	60	0.0	1.8	81.8	16.4
0.50		5	20	1.7	5.2	77.6	15.5
0.25	0.25	5	20	0.0	8.0	78.8	13.1
0.25	0.25	5	20	1.8	5.0	81.0	12.2
0.50	0.50	5	0	2.8	1.2		

The analogous calculation is carried out for the cyclopentadiene fragments[12,21] (*m/e* 66, 67).

$$\text{no. } d_0 = \text{intensity of } m/e \text{ 66} = 100$$

$$\text{no. } d_1 = 68.6 - (5.5\%)(100) = 63.1$$

where 5.5% of *m/e* 66 is the isotopic contribution[37] of *m/e* 66 to *m/e* 67. Thus

$$\%\ d_1 = \left(\frac{63.1}{100 + 63.1}\right)100 = 38.7\%$$

and

$$\%\ \text{IIIb} = \left(\frac{\%\ d_1 \text{ in cyclopentadiene ion fragment}}{\%\ d_1 \text{ in molecular ion}}\right)100 = \left(\frac{38.7}{92.2}\right)100 = 42\%\ \text{IIIb}$$

leaving 58% IIIa. Similar calculations for the experiments involving labeled III corresponding to Table I are given in Table IV. Mass spectral confirmation of labeled III results from observation that *m/e* 130 corresponds to 7.7% of *m/e* 129 due to labeled III plus 32% of the *m/e* 128 peak. The intensity of *m/e* 131 essentially corresponds to 32% of *m/e* 129 due to labeled III.

Stability of II under Reaction Conditions.—Samples of pure II (and I, where indicated) were added (in the amounts as indicated in Table V) to 50 ml of methylene chloride. The resulting solution was treated with hydrogen chloride gas under conditions listed for Table I above and for the times indicated in Table V. The samples were quenched with aqueous sodium carbonate and directly analyzed by pmr spectroscopy. The composition of the mixture was determined by integration of signals known to be due to each of I–IV. A sample of II subjected to these work-up conditions was stable and did not convert to I (by pmr).

Registry No.—I, 121-46-0; II, 278-06-8; III, 3721-19-5; IIIa, 30715-36-7; IIIb, 30715-37-8; IV, 3509-46-4; HCl, 7647-01-0; DCl, 7698-05-7.

Acknowledgments.—Portions of this work were supported by the Research Corporation (grant to Terence C. Morrill) and by NSF-URP (department grant). We would like to thank Drs. E. Krakower and F. Elder of this department for the spectroscopic analyses, and R. E. Gilman for stimulating discussions.

Stereochemistry and Mechanisms of Cyclopropane Ring Cleavage. Addition of Hydrogen Chloride to Tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane-1,5-dicarboxylic Acid (Quadricyclenedicarboxylic Acid)

STANLEY J. CRISTOL[1] AND J. KENNETH HARRINGTON

Department of Chemistry, University of Colorado, Boulder, Colorado 80302

TERENCE C. MORRILL* AND BRIAN E. GREENWALD

Department of Chemistry, Rochester Institute of Technology, Rochester, New York 14623

Received January 7, 1971

Addition of hydrogen chloride to tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane-1,5-dicarboxylic acid (**1**, quadricyclenedicarboxylic acid) under various conditions results in two products, *exo*-5-chlorotricyclo[2.2.1.0^{2,6}]heptane-2,*endo*-3-dicarboxylic acid (**4a**) and *exo*-5-chlorotricyclo[2.2.1.0^{2,6}]heptane-2,*exo*-3-dicarboxylic acid (**4b**). Thus with this cyclopropane ring, cleavage by nucleophile proceeds by inversion and (effective) addition of electrophile proceeds by a combination of retention and inversion. The results are interpreted in terms of a homoconjugate addition process.

Considerable attention has been centered on the stereochemistry of the addition of reagents (EX) to cyclopropanes which proceed by electrophile (E^+) transfer followed by nucleophile (X^-) attack.[2-8] It has been pointed out[2] upon scrutiny of these cases that the stereochemistry of electrophilic transfer can involve retention and/or inversion. Although paths rationalizing this this multiplicity can be understood (Figure 1),[2] the reason for choices among those paths has not been ex-

---

(1) Paper LXXI in the series Bridged Polycyclic Compounds. For the previous paper, see S. J. Cristol and R. Kellman, *J. Org. Chem.*, **36**, 1866 (1971).

(2) S. J. Cristol, W. Y. Lim, and A. R. Dahl, *J. Amer. Chem. Soc.*, **92**, 4013 (1970).

(3) S. J. Cristol and R. T. LaLonde, *ibid.*, **80**, 4355 (1958).

(4) (a) A. Nickon and J. H. Hammons, *ibid.*, **86**, 3322 (1964); (b) J. M. Brown and M. C. McIvor, *Chem. Commun.*, 238 (1969).

(5) R. T. LaLonde, J. Ding, and M. A. Tobias, *J. Amer. Chem. Soc.*, **89**, 6651 (1967).

(6) C. H. DePuy, *Accounts Chem. Res.*, **1**, 33 (1968).

(7) K. B. Wiberg and G. Szeimies, *J. Amer. Chem. Soc.*, **90**, 4195 (1968); **92**, 571 (1970).

(8) (a) J. Meinwald and J. K. Crandall, *ibid.*, **88**, 1292 (1966); (b) A. Nickon, and N. H. Werstiuk, *ibid.*, **89**, 3914 (1967).