Electrophilic Additions to Ethylidenenorbornene and Vinylnorbornene

T. C. SHIELDS
Union Carbide Corporation, Chemicals and Plastics, Research and Development Department, South Charleston, West Virginia 25303

Received October 5, 1970

Electrophilic and free radical additions to 5-ethylidenebicyclo[2.2.1]hept-2-ene and 5-vinylbicyclo[2.2.1]hept-2-ene have been carried out with peracetic acid, hydrogen chloride, and methanol. In contrast to chlorosulfonyl isocyanate, peracetic acid primarily attacks the exocyclic double bond in 5-ethylidenebicyclo[2.2.1]hept-2-ene. Several other electrophilic additions are discussed which demonstrate the unpredictable reactivity of the norbornyl system.

Des additions électrophiles et radicaliques de l'acide peracétique, de l'acide chlorhydrique, et du méthanol ont été faites sur l'éthylidène-5 bicyclo[2.2.1]heptène-2 et sur le vinyl-5 bicyclo[2.2.1]heptène-2. La réaction de l'acide peracétique qui attaque principalement la double liaison exocyclique de l'éthylidène-5 bicyclo[2.2.1]heptène-2 contraste avec celle de l'isocyanate de chlorosulfonyle. Plusieurs autres additions électrophiles qui démontrent la réactivité imprévisible du système norbonyle sont discutées.

Canadian Journal of Chemistry, 49, 1142 (1971)

Additions to norbornenyl olefins have resulted in some unusual rearrangements; the homoconjugated molecule 5-ethylidenebicyclo[2.2.1]hept-2-ene (1) (also called ethylidenenorbornene or EN) however has received relatively little attention. Recent work by Moriconi reports the puzzling fact that chlorosulfonyl isocyanate (CSI) adds exclusively to the norbornenyl ring double bond in dicyclopentadiene (2) and exclusively to the exocyclic double bond in EN (3). This impels us to report our findings with electrophilic additions to norbornenes.

In contrast to the behavior with CSI, peracetic acid treatment of EN results in products of epoxidation (83% yield) of both the ring double bond, **1**, and the exocyclic double bond, **2**, in a 1:6 ratio, respectively (Scheme 1). The *bis* epoxide **3** could be prepared with persistent peracid exposure.

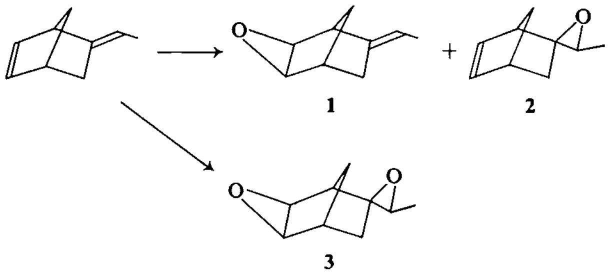
Hydrochlorination of VN requires stannic chloride catalysis. Sodium–ammonia reduction of the products obtained afforded only the anticipated vinylnorbornane. An n.m.r. examination of the mixed hydrochlorides conforms with that of a mixture of *exo*-2-chloro-5 (and -6) vinylbicyclo[2.2.1]heptane (**4**). Three products arise from the reduction of EN hydrochlorides, 1-ethyltricyclo[2.2.1.$0^{2,6}$]heptane (**5**), *endo*-5-ethylbicyclo[2.2.1]hept-2-ene (**6**), and 2-ethylidenebicyclo[2.2.1]heptane (**7**) in a ratio of 3:4:13, respectively.

Three main products arise from hydrochlorination of EN (Scheme 2). Only one, the major product, which was retained longest by g.l.c., was isolated and characterized. Its n.m.r. spectrum agrees with the structure of *exo*-2-chloro-6-ethylidenebicyclo[2.2.1]heptane (**8**). On the basis of their hydrocarbon derivatives the other products are presumed to be *exo*-5-chloro-2-ethyltricyclo[2.2.1.$0^{2,6}$]heptane (**9**) and *exo*-2-chloro-2-ethylbicyclo[2.2.1]hept-5-ene (10); no dichlorides were found. In another experiment using chloroform as solvent the amount of **8** increased to over 80% of the mixture. The predominance of **8** is surprising in light of the earlier findings of Schleyer and O'Connor (4) with hydrochlorination of 5-methylenebicyclo[2.2.1]hept-2-ene in ether in which the tertiary chloride predominated.

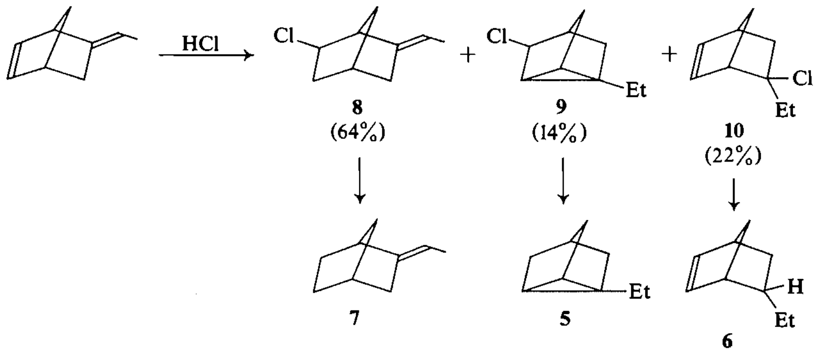
Sulfuric acid catalyzed methanolations were then carried out on EN and VN as well as dicyclopentadiene (5). The products generated were identified easily by n.m.r. and are shown in Scheme 3.

The nortricyclene (**12**) is observed as the main methanolation product from EN. No tertiary ether was isolated; this may be caused by the fact that a second methanolation is possible on the remaining norbornenyl ring double bond of the methoxy analog of **10**. A very small amount of high boiling material (~5%), possible dimethoxy products, were observed by g.l.c.

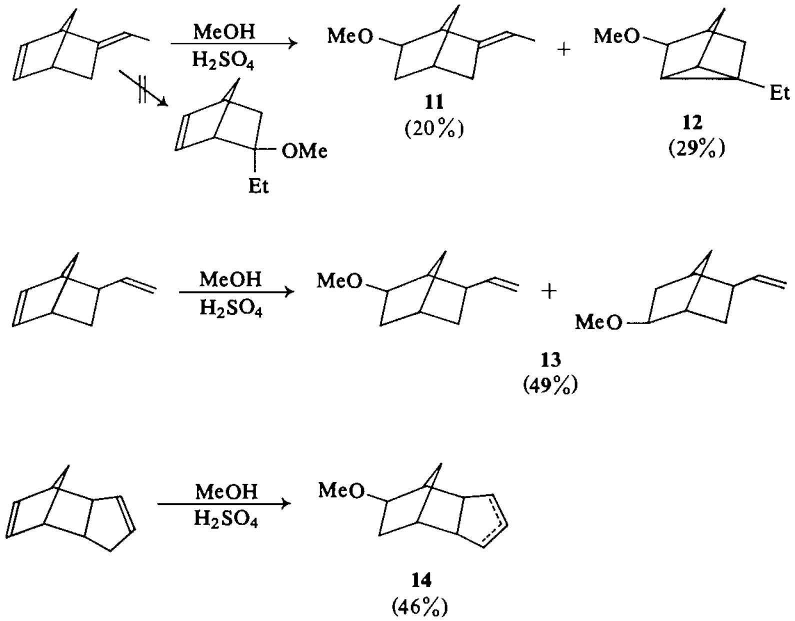
In order to examine the free radical chlorination of EN and VN, treatment with *t*-butylhypochlorite was employed along with irradiation in a paraffin solvent (Scheme 4). The g.l.c. examination of the mixture from VN indicated a complex mixture of at least seven components.



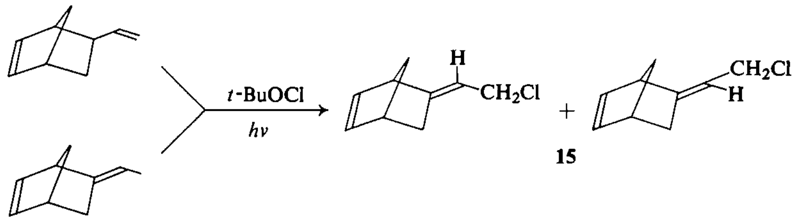
SCHEME 1



SCHEME 2



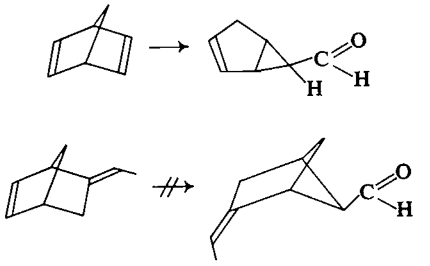
SCHEME 3



SCHEME 4

One component of shorter retention time was isolated by preparative g.l.c. It possesses an n.m.r. spectrum with a narrow multiplet at δ 6.10 (2H, norbornyl olefinic), a multiplet at 5.45 (1H, ethylidene olefinic), a pair of doublets (J = 7.8 Hz) at 4.10 and 3.92 (2H, chlorine geminal), and a complex pattern between 3.60 and 1.10 (6H, alkyl). The ratio of the doublets was variable with different experiments and varied with examination of different distillation crops. These data suggest a mixture of *cis*- and *trans*-2(2′-chloro)ethylidenetricyclo[2.2.1]hept-5-ene (**15**).

The unpredictability of electrophilic additions to norbornyl systems is readily apprehended here. One might expect epoxidation of EN to result in 2-ethylidene-5-formylbicyclo[2.1.1]hexane from a rearrangement analogous to that observed by Meinwald *et al.* (6) with norbornadiene. Instead expoxidation takes place in the normal manner but not exclusively on one double bond.



As previously noted CSI adds exclusively to the exocyclic double bond in EN (2) and the norbornenyl ring double bond in dicyclopentadiene (1). In the case of CSI, mechanistic changes can range from the concerted ($\pi^2s + \pi^2a$) to stepwise electrophilic. In addition dichlorocarbene (a generally accepted electrophilic reagent) adds to the five-membered ring double bond in dicyclopentadiene (7).

The secondary chloride **8** is the main product from EN hydrochlorination; on the other hand treatment of 5-methylene-2-norbornene by hydrochloric acid in ether prepares the tertiary chloride as the main product (4). In contrast to this, methanolation of EN in strong acid results mainly in the nortricyclyl ether **12**. It should also be mentioned that hydrochlorination of EN is quite rapid and spontaneous, presumably because of homoconjugation; however norbornadiene, also homoconjugated, undergoes hydrochlorination far more slowly.[1]

On the basis of these observations one can only say that these electrophilic additions are quite sensitive to reaction environment and subtle changes in substrate; until such time as a consistent, systematic clarification of these phenomena appears, hasty mechanistic supposition in this area should probably be avoided.

Experimental

Materials

Peracetic acid (25% in ethyl acetate), EN (UCC Plant Grade), VN (UCC Plant Grade), hydrogen chloride (Matheson Company CP. 99%), stannic chloride (analyzed reagent), sodium metal, redistilled ammonia, and freshly prepared *t*-butyl hypochlorite were used in the following experiments.

Procedure

General

Boiling points are uncorrected and distillations were performed on a short path column under non-equilibrium conditions. The n.m.r. spectra were taken in CCl_4 unless otherwise noted. Products were quenched with ice water, extracted with pentane, and dried over anhydrous sodium sulfate. Vacuum fractional distillation was employed and the products were isolated on an 8′ silicone gum rubber 10% SE 30 60-80S column between 110–150°. Unless otherwise noted all reactions were carried out in a mechanically stirred, three-neck, round-bottom pyrex flask equipped with nitrogen purge and reflux condenser.

Epoxidations

The EN (50.0 g, 0.417 mol) was dissolved in 100 ml pentane. Peracetic acid (80.2 g, 0.334 mol) was added dropwise at 0° for 3.5 h. The mixture was stirred 1 h longer, quenched, made alkaline with aqueous KOH, and extracted with pentane. Vacuum fractional distillation afforded two cuts; cut A (30–31°/0.8 mm) 34.4 g

---

[1] Unpublished results.

and cut B (33°/0.8 mm) 3.5 g, total yield 37.9 g, 0.278 mol, 83% based on peracid. Isolation of the main constituent, 2,2-methyloxirane-bicyclo[2.2 1]hept-5-ene (**2**) of cut A was accomplished by preparative g.l.c.: n.m.r. δ 6.18 (m, 2H, olefinic), 2.90 (q superimposed on a m, J = 4.3 Hz, 2H), a complex pattern 2.50–1.30 [containing prominences 2.20 (1H), 1.80 (2H), 1.43 (2H)], and 1.15 (d, J = 4.30, 3H, methyl). The i.r. bands appear at 3060, 1265, and 910 cm^{-1}.

Anal. Calcd. for $C_9H_{12}O$: C, 79.36; H, 8.88. Found: C, 79.42; H, 8.57.

The n.m.r. spectrum of cut B shows it contains a 50:50 mixture of epoxides **1** and **2**. This is revealed by the appearance of characteristic olefin patterns at 6.2 (norbornenyl) and 5.3 (ethylidene) in a 2:1 ratio. By the relationships of integrated areas of the two types of olefinic protons in **1** and **2** appearing in cuts A and B a product ratio of 14% **1** and 86% **2** was calculated.

The EN (75.0 g, 0.625 mol) was dissolved in 100 ml pentane at 25° and 75 g peracetic acid added over a period of 1.5 h. The pentane mixture was washed with ice water and made alkaline with a second wash of aqueous base before reintroduction into the reaction flask. Peracetic acid (125 g) was added over a period of 3 h at 45°. After quenching and washing with aqueous base, vacuum fractional distillation afforded cut A (45–56°/0.5–0.3 mm) 12.1 g containing 31% epoxides and 37% *bis*-epoxide and cut B (68 °/0.3 mm) 39.7 g *bis*-epoxide. Yields based on EN, 46.4%, *bis*-epoxide, 4.4% epoxides.

Anal. Calcd. for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: C, 71.34; H, 8.18.

Hydrochlorinations

The EN (48.0 g, 0.40 mol) was exposed to a stream of hydrogen chloride gas at 25° for 1 h. The product was washed with aqueous base and extracted with pentane. Vacuum fractional distillation afforded a mixture (42°/1.5 mm) consisting of 14% (7.6 g) *exo*-5-chloro-2-ethyltricyclo[2.2.1.0^{2,6}]heptane (**9**), 22% (14.1 g) *exo*-2-chloro-2-ethylbicyclo[2.2.1]hept-5-ene (**10**) and 64% (34.9 g) *exo*-2-chloro-6-ethylidenebicyclo[2.2.1]heptane (**8**). Isolation of **8** was accomplished by preparative g.l.c.: n.m.r. δ 5.40 (m, 1H, olefinic), 3.80 (m, 1H, chlorine geminal), 3.20–1.10 (complex pattern 11H, alkyl).

Anal. Calcd. for $C_{10}H_{13}Cl$: C, 69.02; H, 8.31; Cl, 22.67. Found: C, 69.20; H, 8.49; Cl, 22.41.

In a separate reaction employing the same procedure except that 8.0 g EN in 70 ml chloroform was exposed to HCl gas for 2 h, the product ratio changed to 8.5% **9**, 10% **10**, and 81.5% **8**.

Stannic chloride (0.25 ml) was dissolved in VN (38.4 g, 0.32 mol) and hydrogen chloride gas bubbled into the mixture for 10 min. The product was washed with aqueous base and extracted with pentane. Vacuum distillation (37°/1.0 mm) afforded 16.1 g (0.10 mol) of *exo*-2-chloro-5 (and -6) -vinylbicyclo[2.2.1]heptane (**4**): n.m.r. δ 6.20–4.70 (m, 3H, characteristic vinyl pattern), 3.80 (m, 1H, chlorine geminal), 2.60–0.70 (m, 9H, alkyl).

Anal. Calcd. for $C_9H_{13}Cl$: C, 69.02; H, 8.31; Cl, 22.67. Found: C, 69.31; H, 8.13; Cl, 22.53.

Metal–Ammonia Reductions

A mixture of 25.4 g (0.163 mol) EN hydrochlorides was mixed with 20 ml pentane and added dropwise to a solution of 9.0 g sodium in liquid ammonia (177 g). After quenching the mixture excess sodium with NH_4Cl, adding water and extracting with pentane, vacuum fractional distillation (34°/2 mm) of the extract resulted in 18.5 g (0.152 mol, 93% yield) of a mixture of 3 hydrocarbons **4**, **5**, and **6**, in a ratio of 3:4:13 which were all isolated by preparative g.l.c. They were identified as 1-ethyltricyclo[2.2.1.0^{2,6}]heptane (**5**): n.m.r. δ 2.10–0.70 complex pattern with prominences at 1.93, 1.26, 1.10, and 0.85, *endo*-5-ethylbicyclo[2.2.1]hept-2-ene (**6**): n.m.r. δ 6.00 (m, 2H, olefinic), 2.75 (m, 2H, norbornyl bridgehead), 2.10–0.40 (m, 10H, alkyl), and 2-ethylidenebicyclo[2.2.1]heptane (**7**): n.m.r. δ 5.20 (m, 1H, olefinic), 2.60 and 2.45 (m, 2H, norbornyl bridgehead), 2.15–1.0 (m, 11H, alkyl). Elemental analysis was performed on the mixed hydrocarbons.

Anal. Calcd. for C_9H_{14}: C, 88.46; H, 11 56. Found: C, 88.38; H, 11.34.

Similar treatment of VN hydrochlorides (18.0 g, 0.115 mol) rendered 12.1 g (0.10 mol, 89% yield) of one hydrocarbon product which possesses an n.m.r. superimposable on that of 2-vinylbicyclo[2.2.1]heptane.

Methanolations

Hydrocarbon (9.0 g) was dissolved in 50 ml methanol and stirred at 5° while 50 ml 96% sulfuric acid was added from a buret over a period of 20 min. The material was stirred 20 min longer, quenched, and neutralized with aqueous KOH. Pentane extraction and distillation resulted in the following.

(*a*) From EN two major products (**11** and **12**) (31 °/3 mm) arise which were isolated by preparative g.l.c., 5-ethylidene-2-methoxybicyclo[2.2.1]heptane (**11**) (2.26 g, 0.015 mol, 20% yield): n.m.r. δ 5.30 (m, 1H, olefinic), 3.20 (s on m, 4H, oxygen geminal, 2.80–0.80 (m, 11H, alkyl) and 2-ethyl-5-methoxytricyclo[2.2.1.0^{2,6}]heptane (**12**) (3.24 g, 0.021 mol, 29% yield): n.m.r. δ 3.37 (m, 1H, oxygen geminal), 3.20 (s, 3H, methoxy), 2.00–0.70 (m, 13H, alkyl with prominences at 1.90, 1.65, 1.20, 0.98, and 0.88). Elemental analysis was performed on the mixture.

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.14; H, 10.59. Found: C, 78.30; H, 10.48.

Two products of longer g.l.c. retention time comprising ~5% of the total product were not identified.

(*b*) Treatment of VN rendered upon distillation (29–30°/3.0 mm) 5.5 g, 0.036 mol, 49% yield, of 2-methoxy-5 (and -6) -vinylbicyclo[2.2.1]heptane (**13**); n.m.r. δ 5.90–4.70 (m, 3H, characteristic vinyl pattern), 3.21 (s on m, 4H, oxygen geminal), 2.40–0.80 (m, 9H, alkyl).

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.14; H, 10.59. Found: C, 78.07; H, 10.43.

(*c*) Treatment of dicyclopentadiene afforded (48°/1.3 mm) 5.15 (0.031 mol, 46% yield) of *exo*-9-methoxy-*exo*-tricyclo[5.2.1.0^{2,6}]dec-3 (and -4) ene (**14**): n.m.r. δ 5.54 (m, 2H, olefin), 3.19 (s on m, 4H, oxygen geminal), 2.60–1.10 (m, 10H, alkyl). Material has the odor of anise (5).

Anal. Calcd. for $C_{11}H_{16}O$: C, 80.46; H, 9.83. Found: C, 80.26; H, 9.61.

Reaction with t-Butylhypochlorite

The VN (50.0 g, 0.417 mol) in 100 ml pentane was magnetically stirred and the dropwise addition of 21.5 g (0.2 mol) of *t*-butylhypochlorite was carried out over a period of 2 h with a 100 W tungsten lamp irradiating the mixture. Distillation afforded 9.2 g of mixed products. EN (50.0 g, 0.417 mol) treated in a like manner for

2.33 h resulted in 34.9 g of mixed products. Both reaction mixtures contained one product, **15**, in less than 15% yield. Isolation of **15** by preparative g.l.c. was performed. Its n.m.r. spectrum (see Discussion) suggested it to be a mixture of *cis*- and *trans*- 2(2′-chloro)ethylidenebicyclo-[2.2.1]hept-5-ene (**15**).

1. H. E. Fritz, K. E. Atkins, G. L. O'connor. U.S. Pat. No. 3 347 944, October 17, 1967.
2. E. J. Moriconi and W. C. Crawford. J. Org. Chem. **33**, 370 (1968).
3. E. J. Moriconi and C. Jalandoni. J. Org. Chem. **33**, 2073 (1970).
4. P. von R. Schleyer and R. E. O'connor. 134th Meeting, A.C.S. Chicago Illinois, September, 1958. Abstr. p. 39P.
5. L. A. Kheifits and S. I. Virezub. Zh. Obshch, Khim. **34** (6), 2081 (1964).
6. J. Meinwald, S. S. Labana, and M. S. Chadha. J. Amer. Chem. Soc. **85**, 582 (1963).
7. L. Ghosez, P. Laroche, and L. Bastens. Tetrahedron Lett. **49**, 3745 (1964).

The ^{19}F and ^{1}H Nuclear Magnetic Resonance Spectra of 2-Thienylcarbonyl Fluoride and 2-Thiazolylcarbonyl Fluoride

KJELD SCHAUMBURG
Chemical Laboratory V, H. C. Ørsted Institute, DK-2100 Copenhagen Ø, Denmark

Received April 21, 1970[1]

The preparation of 2-thienylcarbonyl and 2-thiazolylcarbonyl fluorides from the corresponding carboxylic acids is described. The n.m.r. spectroscopic parameters are determined and compared with experimental data for similar systems. Theoretical values for the coupling constants have been obtained in the CNDO/2 approximation and they are compared with the experimental data.

Les fluorures des acides thiophènecarboxylique-2 et thiazolecarboxylique-2 ont été préparés à partir des acides correspondants. Les paramètres spectroscopiques (r.m.n.) sont déterminés et comparés avec des valeurs expérimentales trouvées pour des systèmes similaires. Les valeurs théoriques des constantes de couplage obtenues en utilisant l'approximation CNDO/2 sont comparées avec les données expérimentales.

Canadian Journal of Chemistry 49, 1146 (1971)

Introduction

In a growing number of publications, long-range coupling constants in substituted aromatic aldehydes have been cited (1). The carbonyl fluorides constitute a series of molecules with structures closely related to the aldehydes. Recently a correlation between long-range H–H and H–F coupling constants in benzaldehyde and benzoyl fluoride was reported (2). It is our primary aim to investigate if this can be extended to other aromatic systems.

In most cases long-range coupling constants in the aromatic aldehydes have been interpreted in terms of σ–π polarization assuming the σ-contribution to be negligible.

In our calculation of coupling constants we have used the CNDO/2 approximation (3, 4) which only permits calculation of the σ-contribution to the coupling constants. This was done in order to perform calculations of sulfur containing heterocycles on the same level of approximation as for the oxygen and nitrogen containing rings. The present version of the CNDO/2 approximation includes coulomb integrals between occupied and vacant orbitals. Hereby the major part of the correction to the coupling constants obtained by configuration interaction is included. For small molecules of known geometry the coupling constants obtained in this type of CNDO/2 calculation are in better agreement with experimental data than results from simple CNDO/2 calculation. On this basis we have found it of interest to apply the method to the calculation of coupling constants in aromatic carbonyl fluorides.

Experimental Methods and Results

2-Thienylcarbonyl fluoride was prepared according to the method of Yarowenko and Raksha (5) from the corresponding acid. Diethylenglycoldiethylether was used as solvent in the preparation. The yield was approximately 70%. The carbonyl fluoride was distilled into an n.m.r. tube containing diethylenglycoldiethylether as solvent

---

[1] Revision received December 7, 1970.