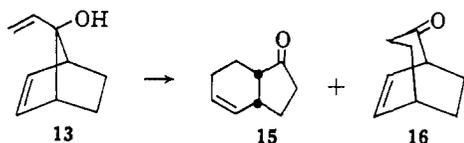


alcohols consumes 2 moles of hydrogen to give 7-ethyl-7-norbornanol,⁶ m.p. 65.5–66.5°, independently prepared from 7-norbornanone and ethylmagnesium iodide. Infrared studies show that the major isomer (**13**) does not have an intramolecular hydrogen bond while the minor isomer (**14**) does. The preference for *syn* addition of the vinyl Grignard reagent to **12** is in accord with the observed¹⁴ course of the reaction of methyl Grignard reagent with **12**.

Pyrolysis of the *syn*-vinyl compound **13** at 250° gives the double-inversion product *cis*-bicyclo[4.3.0]nonen-2-one-7 (**15**)⁶ corresponding to **7**, but this mode of rearrangement now is subordinate (10% of the volatile materials) to the single-inversion path which leads to bicyclo[3.2.2]nonen-6-one-2 (**16**),⁶ m.p. 89–90.8° (84% of the volatile products, 66% isolated yield). An additional 5–6% of minor products is formed.^{12b}



The structure of **16** is established by the infrared spectrum (λ_{\max} 1708 cm^{-1}), by a concordant (but not uniquely decisive) n.m.r. spectrum, and by hydrogenation to 2-bicyclo[3.2.2]nonanone,⁶ m.p. 152.5–154.5°, which is also formed⁹ by pyrolysis of the barium salt of *cis*-4-carboxycyclohexanepropionic acid. Compound **15** can be hydrogenated to *cis*-1-hydrindanone, has an infrared maximum at 1740 cm^{-1} (non-conjugated cyclopentanone), and shows n.m.r. absorptions as multiplets at τ 4.35 (area 2), 7.18 (area 1), and 7.7–8.4 (area 9). Of the seven possible 7-*cis*-bicyclo[4.3.0]nonenones, all but **15**, **17**, and **18** may be eliminated on the grounds of obvious incompatibility with the gross spectral data. The latter two are both mechanistically improbable and furthermore are not in accord with the details of the n.m.r. spectrum, as will be described in the full paper.



The **13** → **16** isomerization provides one of the simplest entries into the bicyclo[3.2.2]nonane system, and the general sequence of vinylation and thermal rearrangement suggests a new synthetic route for conversion of β, γ -unsaturated ketones to bis-homologous δ, ϵ -unsaturated ketones.

(14) R. K. Bly and R. S. Bly, *J. Org. Chem.*, **28**, 3165 (1963).

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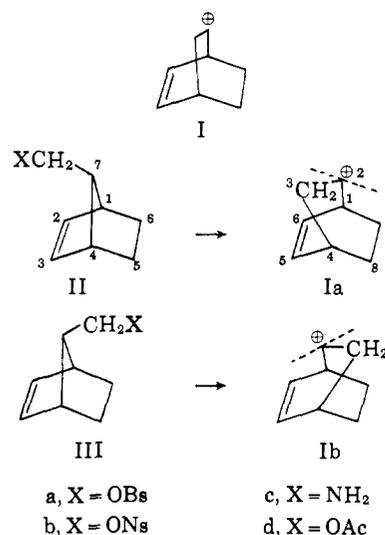
RECEIVED SEPTEMBER 25, 1964

Isomeric Carbonium Ions. Ring Expansion of the *syn*- and *anti*-2-Norbornene-7-carbinyl Systems¹

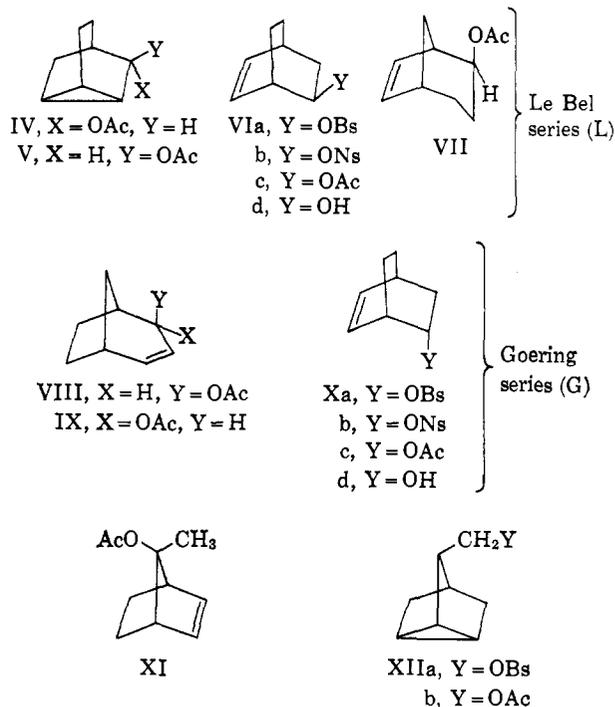
Sir:

The ring expansions² of *syn*-2-norbornene-7-carbinyl derivatives (II) involve intermediates distinctly different from those given by *anti* precursors III.

(1) This work was supported in part by a grant from the Petroleum Research Fund of the American Chemical Society. Grateful acknowledgment



The products of acetolyses (at reflux in the presence of 10–20% excess sodium acetate) of the *p*-bromo- and *p*-nitrobenzenesulfonates (IIa, IIb, IIIa, IIIb) of the *syn* and *anti* series, as well as those obtained from the nitrosative deamination in glacial acetic acid at 25° of the amines (IIc and IIIc),³ fall into three main



categories: (i) the "Le Bel" series (L), IV, V, VIc, VII, previously observed⁴ to result from carbonium

is made to the donors of this fund. We are also indebted for support to the Wisconsin Alumni Research Foundation.

(2) For previous studies of other systems, see J. A. Berson and P. Reynolds-Warnhoff, *J. Am. Chem. Soc.*, **84**, 682 (1962); **86**, 595 (1964); J. A. Berson and D. Willner, *ibid.*, **84**, 675 (1962); **86**, 609 (1964).

(3) (a) Previous studies of the acetolysis of IIa at 115° reported products IIId (91%), XIIb (8%), and the remainder unidentified; IIIa was reported to give 90% IIId, 4% XIIb, and the remainder unidentified.^{3b} Acetolyses of IIa and IIIa (OBs = OTs) were reported to give "essentially unrearranged" products.^{3c} (b) R. K. Bly, R. S. Bly, and J. E. Goldberg, Abstracts, 146th National Meeting of the American Chemical Society, Denver, Colo., Jan., 1964, p. 6C; (c) R. R. Sauers and R. M. Hawthorne, Jr., *J. Org. Chem.*, **29**, 1685 (1964).

(4) (a) N. A. Le Bel and J. E. Huber, *J. Am. Chem. Soc.*, **85**, 3193 (1963). (b) *cf.* R. R. Fraser and S. O'Farrell, *Tetrahedron Letters*, 1143 (1962). (c) Product V, formed in very small yield in our system, was not observed in the previous case but would have escaped detection there if present in comparable amount.^{4a}

ion reactions of *exo*-2-bicyclo[2.2.2]octen-5-yl derivatives (VI); (ii) the "Goering" series (G), VIII, IX, Xc, previously obtained⁵ from *endo*-2-bicyclo[2.2.2]octen-5-yl derivatives (X); (iii) a miscellaneous group including product XI,⁶ apparently derived by hydride shift, product XIIb, derived by protonation-deprotonation, and product IIId or IIIId, derived without rearrangement. The latter material is the single most abundant product in the acetolyses. Preliminary results indicate that the pattern of product selectivity (L vs. G) in aqueous acetic acid deamination (where the rearranged products are largely alcohols), or in aqueous acetolysis, is not substantially different from that observed in glacial acetic acid. It is significant that very little *endo*- or *exo*-2-bicyclo[2.2.2]octenyl products (VI or X) are formed in any of the reactions, even under conditions where they would have survived.⁷

The rearranged portion from the deamination and from both acetolyses with *syn* starting materials (II) contains more G- than L-products, the preference being about 2.5 to 1 in deamination and somewhat higher in acetolysis. Starting materials of *anti* configuration (III) give predominantly L-products of rearrangement; the selectivity in deamination is about 40 to 1, substantially higher than in the *syn* series. The distributions of rearranged products thus cannot be accounted for with the common intermediate I.

One conceivable way of preserving the genetic memory is by stereospecific rearrangement and ion-pair return (IIa or IIb to Xa or Xb, and IIIa or IIIb to VIa or VIb), followed by solvolysis. This route cannot be ruled out for the ROBs and RONs acetolyses, but seems unlikely as the sole mechanism for the nitrosative deaminations, where the role of the counterion presumably would have to be played by molecular nitrogen.

The possibility that the ring expansion is fully concerted with the second step of the rearrangement in each case is remote, since the geometry of both starting systems seems completely unsuited for this. A "partially" concerted mechanism, in which the C-1-C-6 σ -electrons of II or the C-2-C-3 π -electrons of III interact with C-7 *after* C-4 has started its migration to the CH₂ side chain, is conceptually distinguishable only in degree from the simplest formulation, which involves the deformationally isomeric ions Ia and Ib. These readily accommodate the observed specificity:

(5) H. L. Goering and M. F. Sloan, *J. Am. Chem. Soc.*, **83**, 1992 (1961); H. L. Goering, R. W. Greiner, and M. F. Sloan, *ibid.*, **83**, 1391 (1961); H. L. Goering and D. L. Towns, *ibid.*, **85**, 2295 (1963). We thank Professor Goering and Mr. R. Anderson for supplying detailed procedures for the preparation of VIII and IX before publication.

(6) Identified by vapor chromatographic comparison as such and as the alcohol with authentic samples: cf. R. K. Bly and R. S. Bly, *J. Org. Chem.*, **28**, 3165 (1963), to whom we are indebted for a preprint of their paper. The possibility that our product may be the presently unknown epimer of XI cannot yet be ruled out.

(7) (a) Unidentified peaks in the acetate region of the vapor chromatograms account for about 0.5-3.5% of the total area. Another 2-5% of materials of short retention time (probably hydrocarbons) are present. Substantial amounts of other substances, probably diacetates, also are observed in the acetolyses of *anti*-ROBs (IIIa) and *anti*-RONS (IIIb). (b) From *syn*-amine IIc in acetic acid, the L-series, IV, V, VIc, VII, is formed in the approximate relative proportions 56:1:3:0; the G-series, VIII, IX, Xc, is distributed as 43:1:1. From *anti*-amine IIId, the L-series is 187:5:11:1; of the G-products, only VIII is found (in an amount about equal to V), while IX and Xc are present in undetectably small amounts. These distributions are to be compared with those obtained from VIa^{4a} (L-series, 30:0:1.5:1) and Xa⁹ (G-series, 247:1.25:1).

the axis (dotted line) of the empty p-orbital of Ia lies nearly parallel to the C-1-C-7 bond, delocalization of which traps the cation in the Goering system. The geometry of Ib is correspondingly favorable for interaction between C-2 and the C-5-C-6 π -electrons, which generates the Le Bel system. To judge by the specificities, π -trapping in the Ib \rightarrow L-system is more efficient than σ -trapping in the Ia \rightarrow G-system.

Although some drift *within* each series occurs under acetolytic conditions, interconversion of G- to L-series products or *vice versa* is very slow there or under deamination conditions. The crossover observed in acetolysis occurs to at most a minor extent *via* the nortricycylcarbinyl compounds XIIa or XIIb, since these do not give substantial quantities of G- or L-products under the reaction conditions. Thus, the most likely path for crossover is the single twitch by which Ia or Ib can relax to I.⁸

(8) The full paper will consider such subtle questions as whether Ia and Ib represent potential energy minima; whether there is explicative benefit in considering the species as having delocalized three-center bonding involving C-2, C-3, and C-4; and whether the differences in behavior of the II and III systems are attributable to transitory differences in the local environment of cation I rather than to two structurally different cations.

(9) Dow Chemical Company Fellow, 1964-1965.

(10) Inquiries should be directed to this institution.

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RECEIVED AUGUST 10, 1964

Reactions of Olefins with Xenon Fluorides^{1,2}

Sir:

Direct addition of fluorine to olefins is usually difficult to control and is often accompanied by substitution or cleavage of the carbon chain or both.³ The discovery of the xenon fluorides⁴ made available a series of fluorinating agents which appeared particularly attractive for controllable selective fluorinations. Along with our current interests in the chemistry of xenon compounds, we wish to report the reactions of olefins with xenon fluorides.

The three fluorides, XeF₂, XeF₄, and XeF₆, are known to be progressively more reactive as the amount of fluorine in the molecule increases.⁵ They form elemental xenon as the only product which is easily separated from the organic products. Reactions may be carried out in the vapor phase at room temperature, and the problems associated with the use of solvents are thus eliminated.

The apparatus used in these investigations is very similar to that used for the preparation of the xenon fluorides,⁴ being made mainly from nickel or monel.

(1) Work at the University of Chicago was supported by a grant from the U. S. Atomic Energy Commission.

(2) Based on work performed in part at the Argonne National Laboratory under the auspices of the U. S. Atomic Energy Commission.

(3) For example see M. Hudlicky, "Chemistry of Organic Fluorine Compounds," Pergamon Press, New York, N. Y., 1961, p. 68.

(4) (a) H. H. Claassen, H. Selig, and J. G. Malm, *J. Am. Chem. Soc.*, **84**, 3593 (1962); (b) J. L. Weeks, C. L. Chernick, and M. S. Matheson, *ibid.*, **84**, 4612 (1962); (c) J. G. Malm, I. Sheft, and C. L. Chernick, *ibid.*, **85**, 110 (1963); (d) see also review for the preparation in "Noble Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill. 1963, Chapter 2.

(5) N. Bartlett, *Endeavour*, **23**, 3 (1964).