Tetrahedron, 1966, Vol. 22, pp. 2007 to 2014. Pergamon Press Ltd. Printed in Northern Ireland

SYNTHESIS AND REACTIVITY OF SOME 8-SUBSTITUTED TRICYCLO[3.2.1.0^{2,4}]OCTANE DERIVATIVES

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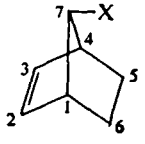
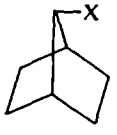
(*Received* 12 *December* 1965)

Abstract—Cyclopropyl formation by addition of methylene units (derived from the cuprous chloride catalyzed decomposition of diazomethane) to 7-norbornadienyl acetate occurs with predominate *exo* addition to the double bond nearer the acetate function. The products are *exo*- and *endo-syn*-tricyclo[3.2.1.0^{2,4}]octen-6-yl 8-acetates (VII and VIII) in the ratio 5 to 1. Reduction of these monoadducts gave *exo* and *endo-syn*-tricyclo[3.2.1.0^{2,4}]octan-8-ols (XIII and XIV). The CuCl–CH_2N_2 reaction with 7,7-dimethoxynorbornene gave exclusively the *exo* isomer (XV), which was converted by hydrolysis and reduction to the *exo-syn* alcohol XIII. The *p*-bromobenzenesulfonate ester of *exo-anti*-tricyclo[3.2.1.0^{2,4}]octan-8-ol underwent acetolysis at 206° with a rate constant of $8{\cdot}0 \times 10^{-5}$ sec^{-1}, indicating that the *exo*-cyclopropyl group has little effect on solvolytic activity in this ring system.

IT IS well known that a cyclopropyl group displays some properties similar to those of a double bond.[1] With regard to the great activating effect of the double bond in acetolysis of *anti*-7-norbornenol derivatives (I) (the ratio of rates in acetolysis of the *p*-toluenesulfonate esters I-*Tos* and II-*Tos* is 10^{11})[2] it is of interest to compare the reactivities of the cyclopropyl compounds III and IV.

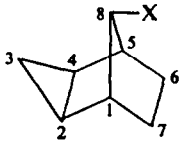


I

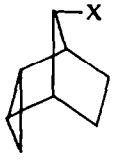


II

In these compounds the double bond of I is replaced by a cyclopropyl group in two possible configurations, *exo* (III) and *endo* (IV).



III



IV

It is generally agreed that with compound I-*Tos* an accelerative interaction of the double bond *p*-orbitals with the developing carbonium ion center at C-7 occurs in

[1] Cf. M. Yu. Lukina, *Russ. Chem. Rev.* (*Eng. trans.*) **31**, 419 (1962); K. B. Wiberg and G. R. Wenzinger, *J. Org. Chem.* **30**, 2278 (1965).

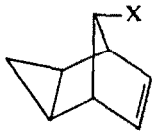
[2] S. Winstein, M. Shatavsky, C. Norton and R. B. Woodward, *J. Amer. Chem. Soc.* **22**, 4183 (1955).

the initial solvolytic step.[3] Since the carbon-carbon bonds of a cyclopropyl group have greater "*p*-character" than do normal unstrained sigma bonds between carbon atoms,[1,6] any interaction of the cyclopropyl orbitals in III and IV (X = sulfonate ester grouping) with a developing carbonium ion should show in their relative rates of acetolysis.[7]

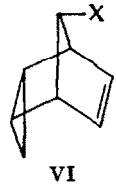
We have investigated the synthesis of these cyclopropyl compounds by the cuprous chloride–diazomethane addition of methylene to *anti*-7-norbornenol and 7-norbornadienyl acetate. We report here the preparation of three of the four isomers of 8-hydroxytricyclo[3.2.1.$0^{2,4}$]octane and the rate of acetolysis of the *p*-bromobenzenesulfonate ester of structure III. However, the isomer of rather special interest (IV) is not available by this method.

RESULTS AND DISCUSSION

The cuprous chloride catalyzed decomposition of diazomethane in the presence of 7-norbornenol gives rise only to the *exo* compounds, alcohol III-*OH* and its methyl ether.[11] The formation of *exo* product in this reaction, as expected from the generally preferred *exo* approach to norbornenyl compounds, has been confirmed by an X-ray structural analysis of the *p*-bromobenzenesulfonate ester of alcohol III.[12] This exclusive *exo* addition is analogous to exclusive *exo* methylene addition to norbornene by the Simmons-Smith reagent (iodomethyl zinc iodide).[13] Since this reagent with norbornadiene gives both *exo* and *endo* addition (ratio 5·7 to 1),[13] it was hoped that compounds V and VI with the desired *exo-anti* and *endo-anti* configurations[14] could be obtained by methylene addition to 7-norbornadienyl acetate.



V



VI

Two monomethylene adducts, as well as a diadduct, were obtained from reaction CH_2N_2–CuCl with 7-norbornadienyl acetate. The NMR spectrum of the mixture

[3] Whether interaction occurs with both *p*-orbitals or with only one *p*-orbital of the double bond in formation of the intermediate ion is still in question.[4,5]

[4] S. Winstein, A. H. Lewin and K. C. Pande, *J. Amer. Chem. Soc.* **85**, 2324 (1963).

[5] H. C. Brown and H. M. Bell, *J. Amer. Chem. Soc.* **85**, 2324 (1963).

[6] See K. B. Wiberg, *Physical Organic Chemistry*, p. 123. Wiley, New York (1964).

[7] The stabilizing effect of direct conjugation of cyclopropyl groups with carbonium ions is well established.[8] A homoconjugative effect of a cyclopropyl group in carbonium ion formation has also been suggested and discussed.[9,10]

[8] N. C. Deno, *Progress in Physical Organic Chemistry* (Edited by S. G. Cohen, A. Streitwieser, Jr., and R. W. Taft) Vol. 2; p. 148. Interscience, New York (1964).

[9] S. Winstein and J. Sonnenberg, *J. Amer. Chem. Soc.* **83**, 3235, 3244 (1961).

[10] E. J. Corey and H. Uda, *J. Amer. Chem. Soc.* **85**, 1788 (1963).

[11] R. E. Pincock and J. I. Wells, *J. Org. Chem.* **29**, 965 (1964). The ca. 10% previously unknown product has now been shown to be the methyl ether of III-*OH*.

[12] A. C. Macdonald and J. Trotter, *Acta Cryst.* **18**, 243 (1965).

[13] H. E. Simmons, E. P. Blanchard and R. D. Smith, *J. Amer. Chem. Soc.* **86**, 1347 (1964).

[14] The term *anti* in the bicyclo[2.2.1]heptene ring system refers to the position of a C-7 group with respect to the double bond (i.e. opposite sides). In the tricyclo[3.2.1.$0^{2,4}$]octenyl ring system an *anti* isomer is defined here as one where the cyclopropyl group is on the opposite side from the C-8 substituent.

of monoadducts showed the olefinic hydrogens as triplets at 3·67 and 4·35 τ (ratio 5 to 1). These resonance positions, shifted from that of *anti*-7-norbornenyl acetate (4·04 τ) are characteristic of the two configurations of the cyclopropyl group in tricyclo[3.2.1.$0^{2,4}$]octenyl compounds.[15–17] The mixture was then an *exo-endo* pair in the ratio 5 to 1.

Removal of the acetate groups with LAH and catalytic hydrogenation of the resulting alcohol mixture gave two saturated monoadduct alcohols (as well as the diadduct alcohol)[19] neither of which was well known[11,12] *exo-anti* isomer III-*OH*. Since the methylene addition had produced a predominate *exo* product, not transformed into the *exo-anti* isomer, then this new product is the *exo-syn* isomer (VII). An activating effect of the acetate group in this diazomethane–cuprous chloride–olefin reaction, similar to that of oxygen functions (alcohols or acetates) in the Simmons-Smith reaction,[9,22] is demonstrated by the preferential formation of this isomer.

The other monomethylene adduct, obtained to a minor extent in the addition to the diene, is assigned the *endo-syn* structure (VIII) rather than the *endo-anti* structure (VI) on the basis that (for the two possible *endo* structures) the activating effect of acetate could possibly extend to the *endo-syn* approach of reagent but not likely to the *endo-anti* approach.[23] Corroboratory evidence of the *endo-syn* structure comes from the NMR spectrum of this product. The presence of clean triplets for the olefinic hydrogen in VIII (as well as in VII) is supporting evidence for the *syn* structures.[24] Norbornenyl derivatives with an *anti* arrangement of olefinic and C-7 hydrogens often show long range coupling between these hydrogens which result in complex

[15] These olefinic hydrogen resonances, shifted downfield and upfield from the resonance positions of the olefinic hydrogens of norbornene, establish the relative positions of the hydrogens with respect to the cyclopropyl ring.[16] In the *exo* compound the olefinic hydrogens are near the plane of the ring (and therefore deshielded); in the *endo* compounds the olefinic hydrogens are farther from the plane and nearer to the center of the ring (therefore shielded).[17]

[16] R. R. Sauers and P. E. Sonnet, *Chem. & Ind.* 786 (1963); K. B. Wiberg and W. J. Bartley, *J. Amer. Chem. Soc.* **82**, 6375 (1960).

[17] The chemical shift of the bridge hydrogen at position eight in this ring system is also dependent on the orientation of the cyclopropyl group. With an *exo* cyclopropyl (as in compounds VII, X, XIII) this bridge hydrogen is ca. 30 c/s farther upfield than in the corresponding *endo* compounds (VIII, XI, XIV). This is as expected from their respective positions above the plane (*exo* compounds) and nearer the side of the plane (*endo* compounds) of the cyclopropyl carbon atoms. These compounds then provide simple examples of large chemical shifts resulting from the magnetic anisotropy of cyclopropane.[18]

[18] Cf. D. J. Patel, M. E. H. Howden and J. D. Roberts, *J. Amer. Chem. Soc.* **85**, 3218 (1963); J. J. Burke and P. C. Lauterbur, *Ibid.* **86**, 1870 (1964); K. Tori and K. Kitahonoki, *Ibid.* **87**, 386 (1965).

[19] The spontaneous rearrangement of the diadduct (IX) to a tetracyclo[3.3.1.$0^{3,8}$.$0^{3,6}$]nonane system, as reported for some related compounds,[20] does not seem to occur with the above compound. The NMR spectra of IX and its derived alcohol (XII), with features similar to the spectra of III-*OAc*, III-*OH* and XIII, are more consistent with the unrearranged [3.3.1.$0^{3,7}$.$0^{6,8}$]nonane structures.[21]

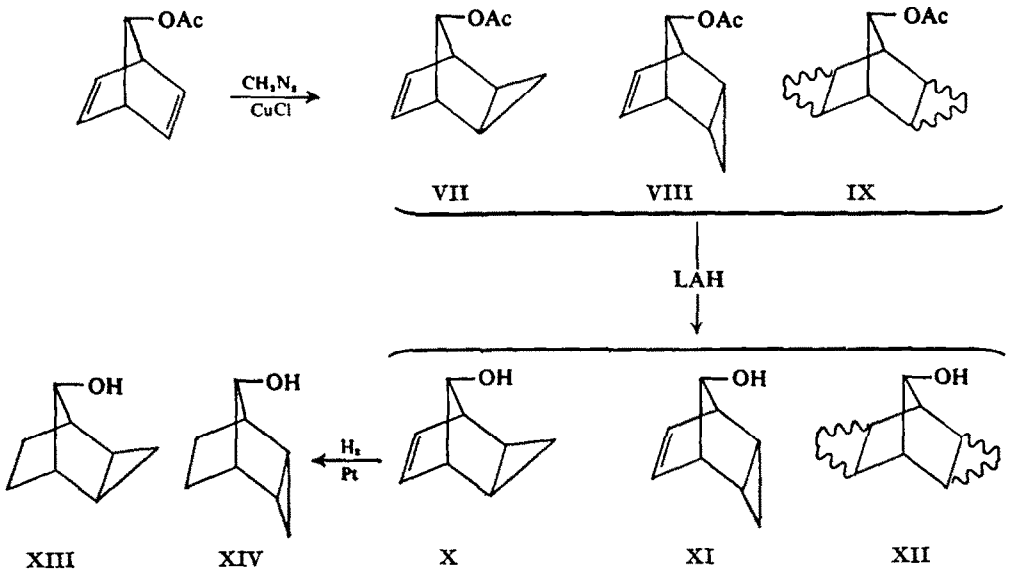
[20] R. A. Baylouny and R. Jaret, *Abstracts, 149th meeting of the American Chemical Society* p. 24P. Detroit, Michigan, April 5–9 (1965).

[21] For photochemical rearrangement of the tricyclo [3.2.1.$0^{3,4}$]octenyl ring system see H. Prinzbach, W. Eberbach and G. von Veh, *Angew. Chem.* (internat. Edit) **4**, 436 (1965).

[22] W. G. Dauben and G. H. Berezin, *J. Amer. Chem. Soc.* **85**, 468 (1963).

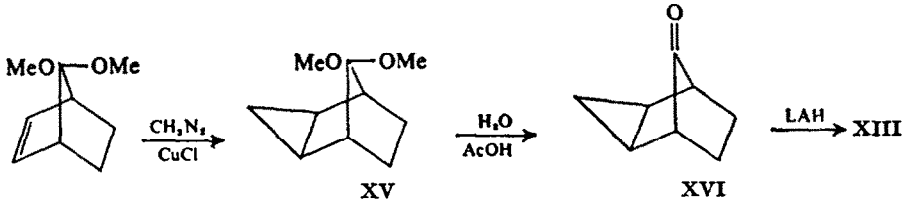
[23] A complexation of Cu with the carbonyl oxygen rather than with the alkoxyl oxygen of the acetate group may be responsible for the *endo-syn* addition.

[24] E. I. Snyder and B. Franzus, *J. Amer. Chem. Soc.* **86**, 1166 (1964); see also J. C. Davis, Jr. and T. V. van Auken, *Ibid.* **87**, 3900 (1965).



multiplets for the olefinic hydrogens. Also the fact that LAH reduction of the product mixture did not result in reduction of the norbornenyl double bond, as it does when C-7 oxygen functions are *syn* to the double bond,[25] strengthens this assignment.

The *exo* compounds, III, VII, X and XIII, have a fixed boat-like conformation in which steric interaction of any large groups on the "bowsprit and flagpole" positions (C-8 and C-3) must occur.[26,27] That *exo-syn* addition to 7-norbornadienyl acetate to give VII is kinetically preferred to relatively less hindered *exo-anti* addition emphasizes the activating effect of the acetate function. Methoxyl groups apparently act similarly. The diazomethane–cuprous chloride methylene addition to 7,7-dimethoxynorbornene proceeds readily and gives only a single product. On hydrolysis this compound was converted to a ketone which gave exclusively the *exo-syn* alcohol XIII when reduced with LAH.[28] This sequence establishes the *exo* configuration of this series. Compounds



[25] For example, *syn*-7-norbornenol gives 7-norbornanol; *anti*-7-norbornenol does not reduce. See B. Franzus and E. I. Snyder, *J. Amer. Chem. Soc.* **87**, 3423 (1965).

[26] E. L. Eliel, N. L. Allinger, S. J. Angyal and G. A. Morrison, *Conformational Analysis* p. 37. Interscience, New York (1965).

[27] From the X-ray structural analysis of compound III-*Bros*[13] the opposed hydrogens on carbon atoms C-3 and C-8, assuming normal 109° and 1·09 Å C–H bond angles and lengths, are about 2·3 Å apart (twice the usually assigned van der Waals radius of hydrogen is 2·4 Å).

[28] This stereospecific hydride reduction of XVI is expected since the reduction of 8-bicyclo[3.2.1]-octanone gives predominantly *syn*-8-bicyclo[3.2.1]octanol. See A. C. Cope, J. M. Grisar and P. E. Peterson, *J. Amer. Chem. Soc.* **82**, 4299 (1960). Reaction on the unhindered side of XVI should then give rise to XIII.

of the tricyclo[3.2.1.0^{2,4}]octenyl ring system are then quite readily obtained by methylene addition to norbornene and norbornadiene derivatives. *Endo* isomers are formed only as minor products and only in addition to norbornadienes.

The availability of the *exo-anti* alcohol allowed an investigation of the solvoytic reactivity of its *p*-bromobenzenesulfonate derivative. Temperatures near 200° were found to be necessary for production of sulfonic acid from III-*Bros* in acetic acid acid containing 0·1*M* sodium acetate. For direct comparison, the rate of acetolysis of 7-norbornyl *p*-bromobenzenesulfonate was also measured at 206°. The cyclopropyl derivative reacts 2·7 times slower than the corresponding 7-norbornyl derivative. The slight rate depressing effect of the *exo* methylene unit in III-*Bros* may be due to steric interference in the solvation of the developing ion at C-8, or the decreased rate possibly arises from the electron withdrawing inductive effect of a cyclopropyl group. In any case, no unusual effect of cyclopropyl in this position with respect to C-8 is observed. The orientation of the *exo* cyclopropyl group in III is such that the *p*-like cyclopropyl orbitals are directed away from the reactive 8-position.[29] However, the sluggish solvolytic property of this *exo*-anti derivative may not be a characteristic of its unknown (as yet) *endo* isomer (IV) where the cyclopropyl ring orbitals are directed towards the C-8 active position.[30] As 7-norbornyl derivatives are exceptionally unreactive and the *exo* compound III-*Bros* even less reactive, any potential long range stabilizing effect of cyclopropyl groups would be distinctive if *endo-anti* compounds turn out to demonstrate considerably enhanced rates of solvolysis.

EXPERIMENTAL[31]

The general procedure used for cyclopropane formation by CuCl catalyzed decomposition of diazomethane in the presence of olefin has been described previously.[11] The progress of a reaction was followed by VPC analysis of the ether solution and the addition of diazomethane was continued until initial olefin was largely consumed.

exo-anti-8-*tricyclo*[3.2.1.0^{2,4}]*octanol* (III-*OH*). This alcohol was prepared from 10·5 g *anti*-7-norbornenol (10·5 g) in the presence of CuCl (1·2 g) by addition of a stream of diazomethane over 12 hr. The previously reported[11] minor product (ca. 10% by VPC analysis on TCEP at 103°) has been identified as *exo-anti*-8-methoxytricyclo[3.2.1.0^{2,4}]octane by comparison of its IR and NMR spectra with an authentic sample prepared as follows.

exo-anti-8-*Methoxytricyclo*[3.2.1.^{2,4}]*octane* (III-OCH_3). Alcohol III (1·0 g; 0·0081 moles), in

[29] For results which demonstrate the preferred arrangement of a cyclopropyl group directly adjacent to a carbonium ion see C. U. Pittman Jr., and G. A. Olah, *J. Amer. Chem. Soc.* **87**, 2998 (1965) and N. C. Deno, J. S. Liu, J. O. Turner, D. N. Lincoln and R. E. Fruit, Jr., *Ibid.* **87**, 3000 (1965).

[30] Some calculations concerning the carbonium ion derived from VI indicate that considerable stabilizing interaction between the *endo* cyclopropyl group and the carbonium ion center at C-8 may occur. See R. Hoffmann, *Tetrahedron Letters* 3819 (1965).

[31] IR spectra were taken on a Perkin–Elmer 137 infracord spectrophotometer. Frequencies are listed in cm^{-1}; w = weak, m = medium, s = strong. Spectra were obtained on neat liquid samples or on nujol mulls of solid samples. All m.ps and b.ps are uncorrected. NMR spectra were obtained on a Varian A-60 spectrometer with resonance frequencies given in τ units, based on tetramethylsilane at 10 τ, in CCl_4 solution; s = broad singlet or unresolved multiplet, m = multiplet, 2 = doublet, etc. All peaks integrated for the correct number of protons unless otherwise stated. Microanalyses were done by A. Bernhardt, Mulheim. Three columns were used for gas chromatographic analyses; a 5 ft 20% Apiezon J on 60/80 mesh firebrick column, a 5 ft 20% 1,2,3-tris(2-cyanoethoxy)propane (TCEP) on 45/60 mesh Chromosorb P column, and a 5 ft 25% Carbowax 20M on 60/80 mesh Chromosorb W (acid washed) column using He as the carrier gas at a flow rate of ca. 42 ml/min. All chemicals used were of reagent grade and used without further purification unless otherwise stated. Column chromatography was done on British Drug Houses chromatographic silica gel.

1,2-dimethoxyethane (10 mc anhydrous glyme) was slowly added to a stirred suspension of NaH (0·4 g; 0·0167 moles) in anhydrous glyme (50 ml) and refluxed for 1 hr. After cooling the reaction mixture to room temp, MeI (3·0 g; 0·0211 moles) in anhydrous glyme (10 ml) was added followed by stirring at room temp for 1 hr. Water and diethyl ether were added to the mixture, the ether layer washed with sat NaClaq, dried with $MgSO_4$ and evaporated to give 0·92 g (82·5%) of III-OCH_3 as a yellowish oil. VPC on TCEP at 80° showed that this ether was identical to the one isolated from the reaction of *anti*-7-norbornenol with diazomethane. IR and NMR spectra confirmed this assignment. B.pt. 184° at 750 mm. (Found: C, 78·11, 78·27; H, 10·16, 10·07; CH_3O, 22·67. $C_8H_{11}OCH_3$ requires: 78·21; H, 10·21; CH_3O; 22·41%.)

IR: 2950 (s), 1120 (s), 1070 (m), 1040 (w), 1005 (w), 995 (w), 955 (w), 900 (w), 880 (w), 810 (m), 745 (m), 710 (w).

NMR: methyl 6·93 (s); bridge 7·00 (m); bridgehead 7·86 (s); *endo*/*exo* 8·4 (m), 8·8 (m); cyclopropyl 9·3 (m) (three protons), 10·1 (m) (one proton).

exo-syn-*Tricyclo*[3.2.1.$0^{2,4}$]oct-6-ene-8-acetate (VII), endo-syn-*tricyclo*[3.2.1.$0^{2,4}$]*oct-6-ene-8-acetate* (VIII) *and tetracyclo*[3.3.1.$0^{2,4}$.$0^{6,8}$]*nonan-8-acetate* (IX). 7-Norbornadienyl acetate, (3·6 g; 0·024 moles), and CuCl catalyst (0·4 g) were reacted with diazomethane for 9 hr using a TCEP column at 130° to monitor the reaction. From the resulting green oil (4·3 g), obtained by filtration and evaporation of the ether solution, was isolated by VPC on the TCEP column at 130° a non-separable mixture of VII and VIII (retention time 27 min), and pure IX (retention time 60 min).

The VPC trace on TCEP at 130° showed that at least two components were present in the mixture of VII and VIII but no VPC column was found that would separate them sufficiently for collection.

The NMR spectrum showed that a 5 to 1 mixture of VII to VIII was present. (Found: C, 72·99; H, 7·57. $C_{10}H_{12}O_2$ requires: C, 73·15; H, 7·37%.)

IR (on mixture): 3100 (w), 3000 (m), 1740 (s), 1600 (w), 1550 (w), 1440 (w), 1360 (m), 1240 (s), 1040 (s), 900 (m), 850 (w), 780 (m), 720 (m), 690 (m).

NMR (VII): olefinic 3·67 (3); bridge 6·05 (s); bridgehead 7·11 (s); acetate 8·11 (l); cyclopropyl 9·0 (m).

NMR (VIII): olefinic 4·35 (3); bridge 5·58 (s); bridgehead 7·65 (s); acetate 8·11 (l); cyclopropyl 9·0 (m).

The liquid acetate (IX) seemed to be pure by VPC on TCEP at 130° but is of unknown stereochemistry. A sample for analysis was separated by VPC. (Found: C, 73·78; H, 7·81. $C_{11}H_{14}O_2$ requires: C, 74·13; H, 7·92%.)

IR: 3000 (m), 2950 (m), 1740 (s), 1450 (w), 1420 (w), 1360 (m), 1320 (w), 1240 (s), 1220 (m), 1170 (w), 1100 (m), 1070 (m), 1040 (m), 980 (m), 910 (m), 860 (w), 820 (w), 790 (m), 770 (w), 710 (m).

NMR: bridge 5·90 (s); bridgehead 7·59 (s); acetate 8·12 (l); cyclopropyl 8·89 (m) (six protons), 9·68 (m) (two protons); other 8·5 (m) (one proton).

exo-syn-*Tricyclo*[3.2.1.$0^{2,4}$]*oct-6-ene-8-ol* (X), endo-syn-*tricyclo*[3.2.1.$0^{2,4}$]*oct-6-ene-8-ol* (XI) *and tetracyclo*[3.3.1.$0^{2,4}$.$0^{6,8}$]*nonan-9-ol* (XII). 7-Norbornadienyl acetate (10·5 g; 0·07 moles), and CuCl catalyst (1·2 g) were reacted with diazomethane for 12 hr as given above, the catalyst filtered off and the ether solution slowly added at room temp to finely divided LAH (6·0 g; 0·159 mole) suspended in magnetically stirred anhydrous diethyl ether (100 ml). After the addition was complete, the reaction mixture was stirred for an additional hr at room temp. Water and ice were added, the resulting aqueous suspension of Al salts separated and the ether solution washed with water, with sat NaCl aq and then dried over $MgSO_4$. Evaporation of the ether gave 7·4 g (86% based on addition of one mole of diazomethane) of a clear, colorless oil.

2·0 g of this oil was separated by column chromatography on 175 g silica gel using as solvent a 2 to 1 mixture of pet. ether (b.pt. 30–60°) to diethyl ether. The column separation, which was monitored by TLC using the same solvent system, gave 3 fractions. The first was separated by VPC on TCEP at 130° into 2 components. The more volatile of these two (retention time 25 min), the predominate product of the reaction, was identified as alcohol (X), m.pt. 33–34° (sealed tube), from its NMR spectrum. (Found: C, 78·39; H, 8·38; O, 13·22. $C_9H_{10}O$ requires: C, 78·65; H, 8·25; O, 13·10%.)

IR: 3300 (s), 3050 (w), 3000 (w), 1650 (w), 1080 (s), 1010 (w), 940 (w), 875 (w), 830 (m), 770 (m), 720 (m), 685 (s).

NMR: olefinic 3·62 (3); hydroxyl 5·95 (l); bridge 6·68 (s); bridgehead 7·18 (s); cyclopropyl 8·9 (m).

The other component of this first fraction was identified as XII (retention time 63 min) of unknown configuration, m.pt. 61–63° (sealed tube). (Found: C, 79·03; H, 9·09. $C_9H_{12}O$ requires: C, 79·37; H, 8·88%.)

IR: 3200 (s), 2900 (s), 1100 (s), 1040 (s), 1030 (m), 970 (s), 925 (m), 855 (w), 805 (m), 785 (s), 750 (w), 690 (s).

NMR: hydroxyl 6·33 (l); bridge 6·67 (m); bridgehead 7·63 (s); cyclopropyl 8·80 (m) (six protons), 9·60 (m) (two protons); other 8·03 (m) (one proton). The appearance of the extraneous peaks in the NMR spectra of both IX and XII may be due to a second isomer.

The second fraction from the column chromatography was further purified by VPC on TCEP at 130° and was unequivocally shown by IR spectral comparison with that of an authentic sample to be 7-norbornenol arising from reduction of unreacted 7-norbornadienyl acetate.

The third fraction was also purified by VPC on the TCEP column at 130° and was identified as XI, m.p. 60–62° (sealed tube). The analysis for the saturated alcohol (XIV) derived directly from this compound establishes this compound as a monomethylene adduct (see below).

IR: 3350 (s), 3050 (w), 2900 (s), 1600 (w), 1220 (s), 1070 (s), 1010 (m), 960 (m), 920 (m), 870 (s), 790 (s), 755 (s), 730 (s), 720 (s).

NMR: olefinic 4·33 (3); bridge 6·2 (s); hydroxyl 7·12 (m); bridgehead 7·42 (s); cyclopropyl 8·58 (m) (two protons), 9·3 (m) (two protons).

Other samples of X, XI and XII were obtained by direct separation of the original reaction mixture by VPC on TCEP at 130°. The ratio of X and XI was estimated from the areas of the VPC tracings to be 5 to 1.

exo-syn-*Tricyclo*[3.2.1.0^{2,4}]*octan-8-ol* (XIII). A crude mixture of X and XII, (0·166 g), was dissolved in 10 ml 95% EtOH, with 0·0155 g PtO_2 added as catalyst, and exposed to H_2 gas at about 1·1 atmospheres. The solution took up 30·0 ml H_2 in a linear fashion over 35 min and took up no more up to 90 min. The catalyst was filtered off and the EtOH evaporated to give 0·146 g of a clear colorless oil. A VPC comparison on TCEP at 130° with the *anti* isomer III-*OH* showed conclusively that the new saturated alcohol was different. This was confirmed by IR and NMR comparisons, m.p. 44–46° (sealed tube). Alcohol X was separated from minor amounts of XII by VPC. (Found: C, 77·58; H, 9·70; O, 12·81. $C_9H_{12}O$ requires: C, 77·38; H, 9·74; O, 12·88%.)

IR: 3350 (s), 2900 (s), 1150 (m), 1080 (s), 1010 (w), 940 (w), 875 (w), 830 (m), 770 (m), 720 (m), 685 (s).

NMR: bridge 6·55 (s); hydroxyl 6·79 (s); bridgehead 7·9 (s); *endo*/*exo* 8·75 (m); cyclopropyl 9·2 (m) (three protons), 10·1 (m) (one proton).

endo-syn-*Tricyclo*[3.2.1.0^{2,4}]*octan-8-ol* (XIV). Crude XI (0·106 g) was dissolved in 95% EtOH (10 ml) with PtO_2 (0·0147 g) added as catalyst. Hydrogen (12 ml) was taken up in 15 min with no further uptake for the next 30 min. After filtration of the catalyst and evaporation of solvent, 0·0816 g of a clear colorless oil remained. A comparison of this oil by VPC on the TCEP column at 120° showed that the main peak was neither of the *exo* isomers (III-*OH*) or XIII. This was confirmed by IR and NMR comparisons, m.p. 125–127° (sealed tube). (Found: C, 77·05; H, 9·64. $C_9H_{12}O$ requires: C, 77·38; H, 9·74%.)

IR: 3300 (s), 2900 (s), 1130 (s), 1060 (s), 990 (w), 930 (w), 800 (w), 780 (m), 750 (w), 720 (s).

NMR: bridge 6·0 (s); hydroxyl 6·32 (m); bridgehead 8·05 (s); *endo*/*exo* 8·6 (m); cyclopropyl 8·9 (m).

exo-8,8-*Dimethoxytricyclo*[3.2.1.0^{2,4}]*octane* (XV). 7,7-Dimethoxynorbornene (2·0 g) and of CuCl (0·36 g) were treated with diazomethane for 6 hr. The reaction mixture was filtered and the ether evaporated to give a green oil. VPC on a TCEP column at 108° showed only one new product (together with some unreacted olefin). For characterization, this product, an oil, was separated by VPC. (Found: C, 71·37; H, 9·68. $C_{10}H_{16}O_2$ requires C, 71·39; H, 9·59%.)

IR: 2950 (s), 1460 (m), 1360 (m), 1300 (s), 1260 (s), 1220 (w), 1200 (s), 1160 (s), 1140 (m), 1110 (s), 1080 (s), 1060 (s), 1040 (m), 1020 (m), 1015 (m), 1000 (w), 980 (m), 940 (m), 870 (w), 810 (s), 790 (w), 755 (s).

NMR: methoxyl 6·88 (s); bridgehead 7·89 (m); exo 8·25 (m); endo 8·68 (m); cyclopropyl ~8·75 (m) (one proton); 9·2 (m) (two protons); 10·0 (m) (one proton).

A sample of this ketal (1·0 g) was hydrolyzed for 25 hr at 70° in AcOH (7·5 ml). The reaction mixture was neutralized with NaOH (6 g) in water (20 ml). The product then extracted into about 4 × 25 ml pet. ether (b.p. 30–60°). Evaporation of the solvent under red. press. gave 0·7 g (96% crude

yield) of a yellowish, slushy oil. VPC on a TCEP column at 120° indicated that this product contained a single product identified as XVI by its spectral characteristics.

IR 2980 (m), 1890 (w), 1790 (s), 1460 (w), 1260 (w), 1150 (w), 1040 (w), 1000 (w), 985 (w), 960 (w), 870 (w), 825 (w), 800 (w), 770 (w), 720 (s).

NMR: bridgehead 8·04 (s); *exo/endo*, 8·23 (s); cyclopropyl, 8·85 (pair of doublets) (two protons), 9·50 (a pair of triplets) (one proton), 9·88 (m) (one proton).

About 0·5 g of this ketone was added slowly to a stirred suspension of excess LAH in ether. After 3 hr at room temp, normal workup yielded an oil which was shown by VPC on TCEP at 135° to contain essentially only the *exo-syn* alcohol XIII. A collected VPC sample of this product was a solid, m.p. 43–46° (sealed tube), confirmed as alcohol XIII by its IR spectrum.

Kinetic procedure. Rates of acetolysis of the *p*-bromobenzenesulfonate esters of *oxo-anti*-8-tricyclo-[3.2.1.0^{3,4}] octanol and of 7-norbornenol were obtained by the general procedure summarized by Bartlett and Giddings.[32] Samples (0·08 M in brosylate, 0·11 M AcONa in AcOH) were contained in individual thick walled glass tubes, and these were placed into small brass bombs for protection against failure of the tubes. The constant temp silicone oil bath was preheated to about 25° above the temp at which the run was to be made in order to offset part of the large temp drop which occurred when the bombs were placed in the bath. About 0·5 hr was allowed for temp equilibration before removing the first sample. Samples were quenched by cooling the tubes. One ml. aliquots of the kinetic samples were added to 10 ml of 0·02 M perchloric acid in AcOH, and 4 or 5 drops of indicator (a saturated solution of bromphenol blue in AcOH) added. These solutions were titrated with standard 0·02M AcONa in AcOH to the first yellow color. With the brosylate ester of III a darkening of the solution, accompanied by deposition of carbon-like material on the sides of the tubes, occurred during the solvolysis. The infinity samples were so dark that the end point could not be determined accurately and theoretical end points were used. Samples could be analyzed, by the above method, to the first halflife and first order plots of the data gave good straight lines. The temps, first order rate constants and initial concentrations of brosylate are as follows: for 7-norbornyl brosylate at 206°, $2{\cdot}97 \times 10^{-4}$ sec^{-1} at 0·077 M,[33] for brosylate ester of III, at 206°, $8{\cdot}15 \times 10^{-5}$ sec^{-1}, $7{\cdot}82 \times 10^{-5}$ sec^{-1} (0·041 M); at 198°, $3{\cdot}43 \times 10^{-5}$ sec^{-1}, $3{\cdot}79 \times 10^{-5}$ sec^{-1} (0·08M); at 163°, $2{\cdot}94 \times 10^{-6}$ sec^{-1} (0·04 M).

Product studies. The products of acetolysis of III-*Bros* at 200° were not fully characterized due to the low yields and complexity of the acetate product mixture. However, the simple substitution product, III-*OAc* was absent in the mixture from complete reaction of III-*Bros* and the lack of cyclopropyl NMR peaks in the crude product mixture showed that cleavage of the cyclopropyl ring had occurred. It is unlikely that this ring cleavage precedes the rate determining formation of sulfonic acid for the following reasons: (1) the rate of sulfonic acid production is slow as expected for a structure related to II, the products expected to be formed by such a ring cleavage would have a much greater rate of brosylate solvolysis[34,35] than the compound of structure III-*Bros*; (2) unrearranged III-*Bros* could be isolated from solutions partly reacted at 200°; (3) The product of direct substitution, i.e. the acetate ester of III, undergoes ring opening in AcONa–AcOH at 200° to give a product mixture *similar* to that of III-*Bros* and (4) rough kinetic measurements show that this ring opening of III-*OAc* is somewhat slower than the titrametric rate of solvolysis of III-*Bros*.

Acknowledgement—We thank the National Research Council of Canada and the Petroleum Research Fund administered by the American Chemical Society for support of this work. We would also like to express our thanks to the Department of Scientific and Industrial Research, U.K., for a fellowship to J.I.W., and to the University of British Columbia and National Research Council for fellowships to J. H-F.

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