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

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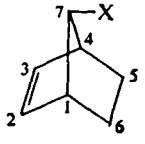
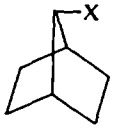
Abstract—Cyclopropyl formation by addition of methylene units (derived from the cuprous chloride catalyzed decomposition of diazomethane) to 7-norbornadienyl acetate occurs with predominate *exo* addition to the double bond nearer the acetate function. The products are *exo*- and *endo-syn*-tricyclo[3.2.1.0^{2,4}]octen-6-yl 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.

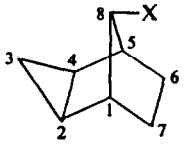


I

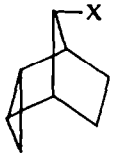


II

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).

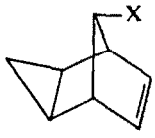
[2] S. Winstein, M. Shatavsky, C. Norton and R. B. Woodward, *J. Amer. Chem. Soc.* **22**, 4183 (1955).

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]

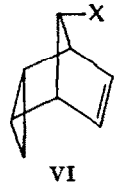
We have investigated the synthesis of these cyclopropyl compounds by the cuprous chloride–diazomethane addition of methylene to *anti*-7-norbornenol and 7-norbornadienyl acetate. We report here the preparation of three of the four isomers of 8-hydroxytricyclo[3.2.1.$0^{2,4}$]octane and the rate of acetolysis 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.