One cubic centimeter of hot 0.3 *M* trichloroacetic acid was added to each sample and the insoluble protein which formed was collected by centrifuging. It was washed three times with 2.5 cc. of 0.1 *M* trichloroacetic acid. Fifty gamma of chymotrypsin produced an insoluble protein containing 3.6 mg. of nitrogen per 0.66 g. of Witte peptone in forty hours. One milligram of chymotrypsin produced insoluble protein containing 9.84 mg. of nitrogen under similar conditions.

The protein synthesizing property of chymotrypsin is of biological importance because under optimum conditions this enzyme displays only weak proteolytic action.

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THE STRUCTURE OF THE BICYCLO[2,2,1]2-HEPTYL (NORBORNYL) CARBONIUM ION

Sir:

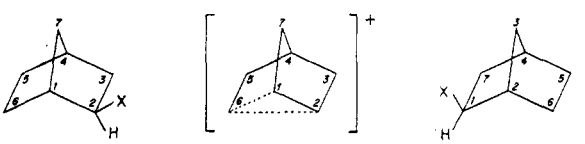
From a generalized viewpoint many rearrangements involve participation of electrons associated with a neighboring β-H,R, or Ar group in a unimolecular-type nucleophilic replacement process. Thus, in the Wagner–Meerwein rearrangement, ionization produces directly, or in a later stage, a rearranged ion or an ion with a bridged structure. The latter type formulation for a carbonium ion has been mentioned a number of times as a possibility or definitely proposed.[1] The same kinetic and stereochemical methods employed in the study of functional neighboring groups[2] are useful in this connection.

In the norbornyl system relative rates of acetolysis at 45° of *p*-toluenesulfonates or *p*-bromobenzenesulfonates are: *exo*-norbornyl (I, III, X = $OSO_2C_6H_4Br$), 350 > *endo*-norbornyl, 1 ≅ cyclohexyl. The driving force[2b] in the stereochemically favorable *exo*-isomer is a substantial fraction of that displayed by isobornyl chloride.

Exo-norbornyl *p*-bromobenzenesulfonate (I, III, X = $OSO_2C_6H_4Br$), m. p. 55.3–57.0°, prepared from *exo*-norborneol (I, III, X = OH), m. p. 127.6–128.5° (reported[3] 128–129°) on acetolysis yields *exo*-norbornyl acetate (I, III, X = $OCOCH_3$) (identified as the *exo*-norbornyl 3,5-dinitrobenzoate, m. p. 103.7–105.0°, reported[3] 105°) with no evidence of any *endo*-norbornyl acetate or norbornylene in the product. Also, *endo*-norbornyl *p*-toluenesulfonate, m. p. 28.1–29 2° yields only the *exo*-norbornyl acetate and *exo*-norbornyl alcohol in acetolysis and hydrolysis (aqueous acetone or dioxane), respectively.

The total resolution of the *exo*-norborneol is still in progress but sufficient resolution has been effected for the type of stereochemical test previously carried out in the case of bromonium ions[2a] and similar species. *Exo*-norborneol, $[\alpha]^{22}D - 1.09°$ (chloroform, c = 10.1), prepared from acid phthalate, $[\alpha]^{23}D + 3.33°$ (chloroform, c = 10.0), and which gives an acetate, $[\alpha]^{23}D + 4.47°$ (acetic acid, c = 5.36), was converted to *p*-bromobenzenesulfonate, $[\alpha]^{25}D \cong + 1.29°$ (initially, in glacial acetic acid, c = 20.08). This *p*-bromobenzenesulfonate acetolyzes (with or without dissolved potassium acetate) to give completely inactive product, the activity of the solution disappearing at roughly the solvolysis rate. Examination of the concentrated product showed more precisely the completeness of the racemization under conditions where the fully survived activity would have been 100–200 times the experimental error.

The facts are at present best accommodated by the formulation of the intermediate ion from *exo*-norbornyl derivatives as II



I II III

which has a plane of symmetry through atoms 4, 5 and 6 and is therefore internally compensated. Attack at C-2 yields the original configuration, I; attack at C-1 yields the enantiomorph, III.

The solvolysis of the *endo*-norbornyl *p*-bromobenzenesulfonate is being subjected to the same kind of stereochemical scrutiny.

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(1) *E. g.* (a) Winstein and Lucas, THIS JOURNAL, **60**, 836 (1938); (b) Nevell, de Salas and Wilson, *J. Chem. Soc.*, 1188 (1939); (c) Watson, "Annual Reports," 197 (1939); 120 (1941); (d) Eyring, *Ind. Eng. Chem.*, **35**, 511 (1943); (e) Dewar, *J. Chem. Soc.*, 406 (1946); (f) Walsh, *ibid.*, 89 (1947); (g) Arcus, *Chemistry and Industry*, 442 (1947).

(2) *E. g.* (a) Winstein and Lucas, THIS JOURNAL, **61**, 2845 (1939); (b) Winstein and Grunwald, *ibid.*, **70**, 828 (1948).

(3) Alder and Rickert, *Ann.*, **543**, 1 (1940).

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