Experimental[2]

***n*-Hexyl Isocyanate.**—A mixture of 135 g. of *n*-hexyl isothiocyanate (0.94 mole) and 460.5 g. of *m*-chlorophenyl isocyanate (3 moles) was heated together in a 1-l. single-necked flask provided with a thermometer well. A short, glass-helices-packed fractionating column was used to separate the product isocyanate.

In 15 min., the reaction mixture reached 213°. In 45 min. a head temperature of initially 169° was recorded. The fractionated column was operated at total reflux until a constant temperature of 161° was reached (lit.[3] 162–163°). The product distilled over a 10-hr. period at 163–164°. The reaction temperature meanwhile increased to 230°. A total of 77.5 g. of *n*-hexyl isocyanate was obtained for a 61% yield.

The product showed a strong –NCO infrared absorption peak at 4.4 and secondary peaks at 6.9 and 7.45 μ. The charge stock, *m*-chlorophenyl isocyanate, had peaks at 4.45 and at 6.33 μ. The charge stock, *n*-hexyl isothiocyanate, had a very pronounced –NCS peak at 4.79 and a secondary peak at 4.59 μ.

Allyl Isocyanate. A.—A 99-g. sample of allyl isothiocyanate (1 mole) and 365 g. of *o*-chlorophenyl isocyanate (3 moles) were treated similarly. The initial reaction temperature was 189°. The column was operated at total reflux for 20 hr.; then 18.7 g. of allyl isocyanate was distilled at 84–86° over 6.5 hr. At the end of this time, reflux had become negligible and the reaction temperature had reached 247° to yield 22.5%, lit.[4] b.p. 82°. The reaction bottoms were then vacuum stripped and found to be free of unchanged allyl isothiocyanate. After distillation of 12 g. of *m*-chlorophenyl isocyanate, the residual bottoms were submitted for infrared analysis. The spectrogram clearly revealed absorption bands at 4.73–4.87 μ, corresponding to *m*-chlorophenyl isothiocyanate. No bands corresponding to uretidine diketones were observed. A distinct and typical trimer (isocyanurate) band at 5.81 μ was obtained. Similar bands were obtained at 6.25–6.35 μ, which are probably attributable to thioisocyanurate groups.

B.—A 99-g. sample of allyl isothiocyanate (1 mole) and 261 g. of toluene diisocyanate (3 equiv.) were treated similarly. After 1-hr. reflux, the product was distilled at 84–86° over 2 hr. to yield 19.1 g. (23%). A polymeric mass remained in the reaction flask.

2-Methylallyl Isocyanate.—A mixture of 113 g. of 2-methylallyl isothiocyanate (1 mole) and 3 equiv. of toluene diisocyanate were used. A total of 31 g. of 2-methylallyl isocyanate (31%) was obtained at a boiling range of 107–109°.[5] Infrared spectrum revealed a very strong peak at 4.4 μ corresponding to –NCO.

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[2] Boiling points are uncorrected. Infrared spectra were obtained with a Perkin-Elmer dual beam Infracord.

[3] G. Schroeter, *Ber.*, **42**, 3358 (1909).

[4] A. Cahours and A. W. Hoffmann, *Ann.*, **102**, 297; Beilstein, IV, p. 214.

[5] J. W. Eastes and T. F. Cooke, U. S. Patent 2,699,440 (Jan. 11, 1955).

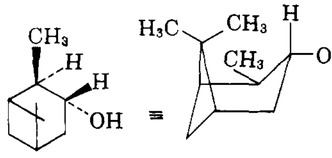
Solvolysis of Iso- and Neoisopinocampheyl Sulfonate Esters. Stereochemical Considerations

FRANK J. CHLOUPEK AND GEORGE ZWEIFEL[1]

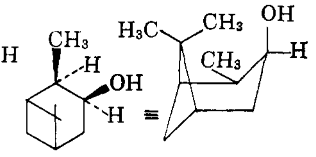
Department of Chemistry, Purdue University, Lafayette, Indiana

Received February 17, 1964

Recently, Schmidt's[2] configurational assignment of isopinocampheol (I) has been challenged.[3,4] It was proposed that the alcohol belongs to the *cis*-pinane series, but the hydroxyl and the methyl group are in a *cis* relationship (II). The arguments were based on conformational analysis,[3] and on the fact that the tosylate solvolyzed extremely fast, pointing to considerable assistance to ionization.[4] Unfortunately, the authors failed to extend the study to neoisopinocampheyl tosylate, to which Schmidt assigned the extreme *cis* configuration (II). An extreme *cis* configuration for the isopinocampheol is in contradiction to the configuration deduced from the hydroboration of α-pinene with diborane.[5] It has been shown that hydroboration of α-pinene occurs *cis* and from the less hindered side of the molecule. Since oxidation of the organoborane occurs with retention of configuration, the alcohol obtained should have the hydroxyl and the methyl group in a *trans* relationship (I).



I



II

In view of these facts it appeared desirable to synthesize neoisopinocampheol and compare the rate of solvolysis of its sulfonate ester with that of isopinocampheol. The neoisopinocampheol (II) was prepared by oxidation of isopinocampheol to isopinocamphone, followed by reduction of the ketone with lithium trimethoxyaluminohydride.[5] The physical constants of the neoisopinocampheol obtained agreed with those reported by Schmidt.[2]

The methanesulfonate esters of the two alcohols were solvolyzed in methanol at 25°. The results are summarized in Table I.

TABLE I

RATES OF SOLVOLYSIS OF CYCLOPENTYL-, ISO-, AND NEOISOPINOCAMPHEYL SULFONATE ESTERS

Compound	Solvent	$k_{25} \times 10^6$, sec.$^{-1}$	Relative rate
Cyclopentyl methanesulfonate	Methanol	5.58	1
Cyclopentyl tosylate	Ethanol	4.96^{a,b}	
Isopinocampheyl methanesulfonate	Methanol	20.2	3.6
Isopinocampheyl tosylate	Ethanol	12.6^{a,c}	
Neoisopinocampheyl methanesulfonate	Methanol	58.5	10.0

[a] The rate was determined at 30°. [b] W. Hückel, *et al.*, *Ann.*, **624**, 142 (1959). [c] See ref. 4.

The results obtained indicate that isopinocampheyl methanesulfonate solvolyzes 3.6 times faster than the cyclopentyl ester. Moreover, the neoisopinocampheyl ester solvolyzes 2.5 times faster compared with the isopinocampheyl derivative.

Consequently, if the rate of solvolysis reflects the spatial relationship between the methyl and the hydroxyl group, the data in Table I support the contention that the hydroxyl and the methyl group have a *cis* relationship in neoisopinocampheol, and a *trans* relationship in isopinocampheol.

Experimental

Isopinocampheyl Methanesulfonate.—To 25 ml. of pyridine was added 2.84 g. of isopinocampheol[5] [20 mmoles, m.p. 55–57°, $[\alpha]^{20}$ −32.8° (*c* 10, benzene)]. The solution was cooled to 0° and 2.29 g. of methanesulfonyl chloride (20 mmoles) was added.

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[1] Chemistry Department, University of California, Davis, Calif.

[2] H. Schmidt, *Ber.*, **77**, 544 (1944).

[3] K. Bose, *J. Org. Chem.*, **20**, 1003 (1955).

[4] W. Hückel and D. S. Nag, *Ann.*, **645**, 101 (1961).

[5] H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 2544 (1961).

The reaction mixture was maintained at 0° for 24 hr., then poured into a mixture of equal volumes of 6 *N* hydrochloric acid and ether. The sulfonate ester was extracted with ether and the ether extract was washed with ice-cold 6 *N* hydrochloric acid. In order to remove traces of pyridine the ether extract was washed once with 10% cadmium chloride solution and dried over anhydrous magnesium sulfate. The ether was removed and the residue crystallized from a mixture of pentane–ether (10:1) at −70°. The isopinocampheyl methanesulfonate had m.p. ~10°. The compound was stable when kept below 0° for a long period of time.

Anal. Calcd. for $C_{11}H_{20}SO_3$: C, 56.90; H, 8.65. Found: C, 56.79; H, 8.73.

Neoisopinocampheyl Methanesulfonate.—Under similar experimental conditions as described above, 0.71 g. of neoisopinocampheol[5] [(5 mmoles, m.p. 45–47°, $[\alpha]^{20}$ +36° (*c* 3, benzene)] was converted to the neoisopinocampheyl methanesulfonate, m.p. ~0°. The compound is less stable as compared to the isopinocampheyl derivative.

Anal. Calcd. for $C_{11}H_{20}SO_3$: C, 56.90; H, 8.65. Found: C, 56.41; H, 8.07.

Rate Studies.—The reaction rates were followed by conventional titrimetric procedures. The first-order reaction constants obtained are summarized in Table I.

Organoboron Compounds. XVI. An Improved Method for the Preparation of Trialkylboroxines[1,2]

PATRICK A. MCCUSKER AND JOHN H. BRIGHT

Department of Chemistry, University of Notre Dame, Notre Dame, Indiana

Received December 3, 1963

The reaction of boric oxide with trialkylboranes was reported earlier[3] to provide a more convenient method for the preparation of trialkylboroxines than the previously used dehydration of alkylboronic acids. Because of the high temperatures and long heating times required, this reaction was restricted to the preparation of primary trialkylboroxines, since thermal isomerization[4] of secondary or tertiary alkyl groups to primary groups occurred during reaction and, as more recently observed,[1] partial conversion of primary alkyl groups to secondary alkyl groups also took place. Furthermore it was found on continued use of this reaction that it was difficult to obtain or prepare samples of anhydrous boric oxide with reproducible reaction characteristics. Incompletely dehydrated boric oxide causes some hydrolysis of trialkylboranes, and boric oxide thoroughly dehydrated at high temperature was found to be very unreactive, resulting in heating times as long as 60 hr. in some instances.

A modification of the method, involving the use of trimethoxyboroxine as a source of reactive boric oxide, with resultant decrease of time of reaction, lower reaction temperatures, and decreased thermal isomerization is reported in the present paper.

Trimethoxyboroxine, obtainable from the reaction of boric oxide with trimethoxyborane (and also available commercially from the Callery Company) is dissociated on attempted distillation[5–7] into boric oxide and trimethoxyborane.

Under controlled conditions it has been found that heating of mixtures of primary trialkylboranes and trimethoxyboroxine as low as 131° and for periods as short as 2 hr. results in 60–77% yields of isomer-pure, sharp-boiling trialkylboroxines. An essential feature of the reaction conditions is that the trimethoxyborane formed by decomposition of trimethoxyboroxine must be distilled as rapidly as it is formed. If the mixture is heated without rapid removal of the trimethoxyborane, the reaction products consist mostly of dialkylmethoxyboranes and alkyldimethoxyboranes resulting from the reaction of trimethoxyborane with trialkylboranes.[8]

In order to determine whether any of the alkyldimethoxyborane, obtained as a by-product in the preparative reaction, resulted from direct reaction between trimethoxyborane and trialkylboroxine, this possible reaction was attempted under the same conditions as used for the preparative reaction. It was found that under these conditions only a 6% yield of alkyldimethoxyborane was obtained.

Of the three reactions involved in the process, the most rapid is apparently the thermal decomposition of trimethoxyboroxine. This follows from the observation that trimethoxyborane can be removed from the reaction mixture in almost quantitative yield by distillation. This requires that reaction of trimethoxyborane with trialkylborane and reaction of boric oxide with trialkylborane be relatively slow. Of the latter two reactions, the trimethoxyborane–trialkylborane reaction appears to be the more rapid since the yield of esters is higher than the yield of trialkylboroxine when the trimethoxyborane is left in the reaction mixture.

The rapid formation of trialkylboroxines at relatively low temperature led to the expectation that isomer-pure secondary trialkylboroxines could be obtained by this method. This expectation was realized in the case of the preparation of tri-*sec*-butylboroxine although it was found that during the preparative reaction some isomerization of secondary to primary groups occurred. From the reaction mixture there was obtained a 35% yield of isomer-pure tri-*sec*-butylboroxine. The total yield of tributylboroxine was 69%. In the case of the treatment of triisopropylborane with trimethoxyboroxine heating for 1 hr. in the same temperature range as for tri-*sec*-butylborane and removal of trimethoxyborane resulted in the precipitation of solid boric oxide but no formation of tripropylboroxine. Heating of the reaction mixture for an additional hour resulted in dissolution of the boric oxide and formation of tripropylboroxine which consisted of an inseparable mixture of normal and isopropylboroxines. It appears that direct reaction of triisopropylborane with trimethoxyboroxine does not occur, while direct reaction of tri-*sec*-butylborane with trimethoxyboroxine does take place under essentially the same conditions. The reason for this difference in behavior is not immediately evident.

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[1] Previous paper: P. A. McCusker, F. M. Rossi, J. H. Bright, and G. F. Hennion, *J. Org. Chem.*, **28**, 2889 (1963).

[2] Contribution from the Radiation Laboratory operated by the University of Notre Dame under contract with the Atomic Energy Commission.

[3] G. F. Hennion, P. A. McCusker, E. C. Ashby, and A. J. Rutkowski, *J. Am. Chem. Soc.*, **79**, 5179 (1957).

[4] G. F. Hennion, P. A. McCusker, E. C. Ashby, and A. J. Rutkowski, *ibid.*, **79**, 5190 (1957).

[5] J. Goubeau and H. Keller, *Z. Anorg. Allgem. Chem.*, **267**, 1 (1951).

[6] G. L. O'Connor and H. R. Nace, *J. Am. Chem. Soc.*, **77**, 1578 (1955).

[7] M. F. Lappert, *J. Chem. Soc.*, 2790 (1958).

[8] R. Koster, *Angew. Chem.*, **71**, 31 (1959).