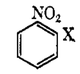
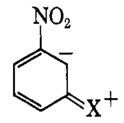
Table III

	Cyclohexanol		Dioxane				Methanol			
	$^1L_a{}^a$	$^1L_b{}^a$	$^1L_a{}^a$	ΔE	$^1L_b{}^a$	ΔE	$^1L_a{}^a$	ΔE	$^1L_b{}^a$	ΔE
NH_2	270 (3.44)	379 (3.54)	276 (3.27)	−2.31	400 (3.28)	−3.96	275 (3.43)	−1.93	398 (3.44)	−3.60
OCH_3	250 (3.67)	305.5 (3.53)	255.5 (3.75)	−2.47	320 (3.55)	−4.24	257 (3.73)	−3.12	321 (3.50)	−4.53
CH_3	250 (3.84)		254 (3.73)	−1.80			255 (3.69)	−2.24		
OH	273 (4.30)	348 (3.76)	276 (4.25)	−1.14	351 (3.96)	−0.70	274 (4.07)	−0.38	351 (3.80)	−0.70
$NHCOCH_3$	275 (3.90)	354 (3.80)	276 (3.89)	−0.38	355 (3.78)	−0.23	270	+1.92	340 (3.73)	−3.33

[a] Wave lengths in mμ (log ε).

rather than the inductive order as for the ^1L_a band. This may be due to greater solvation of excited state forms such as



in which the charge appears on the bond[9] and would contribute more to the low intensity ^1L_b band.

Experimental

Absorption spectra in the region 220–400 mμ were obtained using a Bausch and Lomb automatic recording ultraviolet spectrophotometer, Model 505, with a constant 5-Å. band width and 1-cm. matched silica cells. The spectra were run in Spectroquality solvents (Matheson Coleman and Bell), using concentrations of 1.1×10^{-5} to 7.2×10^{-5} mole/l. and a scan time of 10 min. For those compounds which could undergo association in cyclohexane (*i.e.*, the nitrobenzoic acids), determinations were carried out at concentrations below which no change in the absorption maxima was observed (usually absorbancy values of 0.2 to 0.3). After each series of determinations the instrument was calibrated against the 253.7- and 313.1-mμ lines of mercury.

The nitrobenzenes were purchased as the highest purity compounds available and in some cases were further purified by recrystallization or distillation until the physical constants agreed with literature values. Each compound was then dried for a period of 3–24 hr. in an Abderhalden apparatus. Those compounds not available commercially (*p*-nitro-N,N-dimethylaniline, ethyl *p*-nitrobenzoate, and ethyl *m*-nitrobenzoate) were synthesized by methods listed in "Organic Syntheses" or "Beilstein."

Acknowledgment.—The work of Mr. Jorge Olguin was supported in part by a National Science Foundation Undergraduate Research Participation grant.

Exchange Reaction of Isocyanic Acid Esters and Isothiocyanic Acid Esters

W. E. Erner

Carwin Chemical Company, North Haven, Connecticut

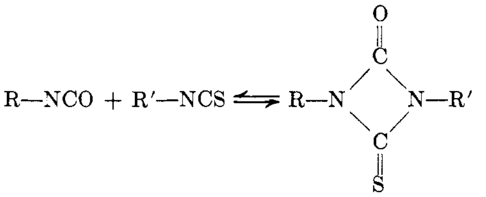
Received February 24, 1964

Isocyanic acid esters and isothiocyanic acid esters have been found[1] to undergo an exchange reaction when simply heated together at temperatures in the range of 190–230°. This exchange reaction has been taken

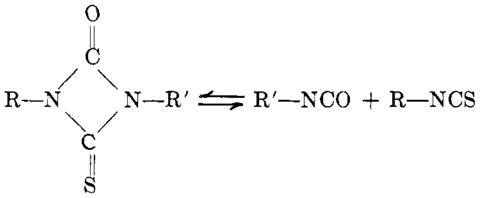
$$R{-}NCO + R'{-}NCS \rightleftharpoons R'{-}NCO + R{-}NCS \qquad (1)$$

advantage of to prepare isocyanates from isothiocyanates. Since isocyanates boil appreciably lower than corresponding isothiocyanates, separation of the desired isocyanates conveniently was achieved by conducting the reaction in the stillpot of a fractionating column. In this manner *n*-hexyl isocyanate was prepared from *n*-hexyl isothiocyanate and *m*-chlorophenyl isocyanate in 61% yield. Allyl isocyanate was obtained in yields of 22.5 and 23% from allyl isothiocyanate and toluene diisocyanate (80% 2,4-; 20% 2,6-) and *o*-chlorophenyl isocyanate, respectively. Similarly, 2-methylallyl isocyanate was obtained in 31% yield from 2-methylallyl isothiocyanate and toluene diisocyanate.

Case proposed that this exchange reaction proceeds through the intermediate formation of uretidinethione ketones.



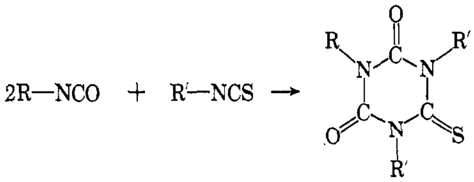
(2)



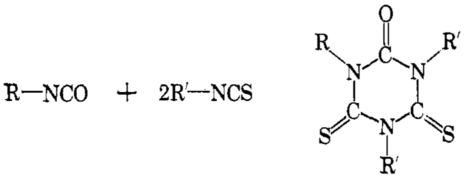
(3)

The marked difference in yield between the allylic isocyanates and the alkyl isocyanates points to competitive reactions. Vinyl polymerization of the allyl groups is not believed to be a significant factor, owing to the nearly identical yields of allyl isocyanate in exchange with toluene diisocyanate and with *m*-chlorophenyl isocyanate, in spite of the markedly different reaction times (2 hr. *vs.* 26.5 hr.).

Trimerization reactions leading to essentially irreversible formation of thio- and dithioisocyanurates are believed to be the major competitive reactions.



(4)



(5)

---

[1] L. C. Case, *Nature*, **183**, 675 (1959).

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.

---

[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).

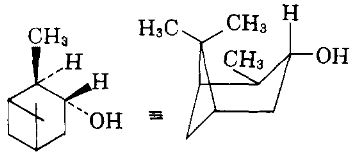
Solvolysis of Iso- and Neoisopinocampheyl Sulfonate Esters. Stereochemical Considerations

Frank J. Chloupek and George Zweifel[1]

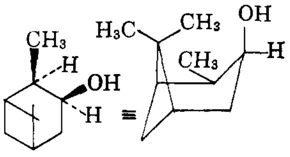
Department of Chemistry, Purdue University, Lafayette, Indiana

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.

---

[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).