

attached to albumin, this partial dissociation may be observed as a decrease of the fluorescence polarization due to the shorter rotational relaxation times of subunits (Fig. 3, cf. Refs. 2 and 10). Radiation-induced structural changes will be detectable as deviations from the normal titration curve provided the reproducibility of values obtained with the instrument is satisfactory. Measurements such as those summarized in Fig. 3 (cf. Weber,<sup>2</sup> Weber

method like gel filtration is complemented with polarization measurements. The results of those investigations will be published elsewhere.

*Acknowledgements.* This project was supported by grants from the *Swedish Atomic Research Council* and the *Faculty of Mathematics and Natural Science*, University of Stockholm.

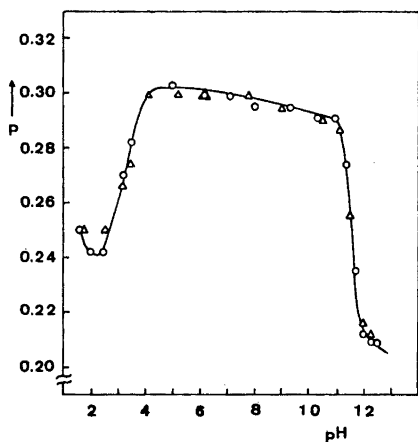


Fig. 3. Polarization of fluorescence as a function of pH for 1,5-dimethylaminonaphthalene-sulfonate conjugated with bovine serum albumin. Different symbols signify measurements on different occasions of identical samples.

and Young<sup>11</sup>) show that our instrument well satisfies such requirements.

We have made a series of experiments, in which solid bovine serum albumin has been  $\gamma$ -irradiated and then fractionated on Sephadex G-100. One difficulty in the evaluation of the yields of such changes as cross-linking and fragmentation by means of gel filtration or ultracentrifugation techniques is that such separations are disturbed by increases of the cross-sections of the molecules due not only to intermolecular cross-links but also to unfolding of the peptide chains. Fluorescence polarization measurements will among other things distinguish between such phenomena. Experiments we have made show that a clearer picture of radiation effects in proteins is obtainable if a separation

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Received June 2, 1970.

### 3-Exoamino-2-endohydroxybornane

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Preparations of three out of four 3-amino-2-hydroxybornane isomers have recently been described in two independent publications.<sup>1,2</sup> However, attempts to prepare the title compound (2) were reported to be unsuccessful.

The synthesis of compound 2 and of the *cis* endo isomer 3 has been accomplished as follows:

**3-Exoamino-2-endohydroxybornane.** 2-Endo-hydroxy-3-hydroxyiminobornane\* (1) [m.p. 174–176°;  $[\alpha]_D^{25} +181.5^\circ$  (c 0.96; ethanol); *m/e* 183 ( $M^+$ ) ( $C_{10}H_{17}NO_2$ ); Found: C 65.6; H 9.4; N 7.5.  $C_{10}H_{17}NO_2$  requires C 65.5; H 9.4; N 7.6], was reduced with Na-amalgam (2%) in water at 70° for 4 h. Carbon dioxide was passed through the solution during the reaction. After working up the reaction mixture the acid soluble fraction gave an amino alcohol mixture in 82% yield containing (NMR) 2 and 3 in a ratio of ca. 3:1. Steam distillation



1.  $RR_1 = NOH$
2.  $R = NH_2, R_1 = H$
3.  $R = H, R_1 = NH_2$

removed the *cis* isomer (3) and after addition of dilute NaOH and subsequent ether extraction the residue afforded the *trans* isomer (2). [M.p. 216–218° (recrystallized from hexane); *m/e* 169 ( $M^+$ ) ( $C_{10}H_{19}NO$ ); NMR ( $CDCl_3 + D_2O$ )  $\delta$  (ppm, TMS): 3.78 (br d  $J = 3.5$  Hz, 1 H,  $CH-OH$ ), 2.51 (br d  $J = 3.5$  Hz, 1 H,  $CH-NH_2$ ), 1.02 (s, 3 H,  $CH_3$ ), 0.87 (s, 6 H,  $CH_2, CH_3$ )]. **Hydrobromide:** [M.p. 298°;  $[\alpha]_D^{25} +21.8^\circ$  (c 0.62; ethanol). Found: C 48.1; H 7.9; Br 32.2; N 5.6.  $C_{10}H_{20}BrNO$  requires C 48.0; H 8.1; Br 31.9; N 5.6].

**3-Endoamino-2-endohydroxybornane.** The *cis* isomer (3) was obtained from the distillate by the same procedure and gave NMR data in complete agreement with those published<sup>1</sup> [m.p. 170–172° (lit.<sup>2</sup> 170–171°)].

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Received June 5, 1970.

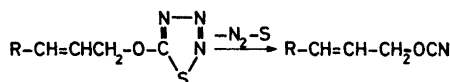
\* The parent ketol was prepared from (+)-camphor; see Ref. 3. Melting points are uncorrected.

## Formation of 1-Methylallyl and 2-Butenyl Isocyanate from Crotyl Bromide and Silver Cyanate

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In a previous paper, attempts to prepare 2-alkenyl cyanates from 5-(2-alkenyl-oxy)-1,2,3,4-thiazotriazoles were described.<sup>1</sup> Although alkyl cyanates are formed when 5-alkoxy-1,2,3,4-thiazotriazoles decompose at room temperature, only isocyanates were isolated from the 5-(2-alkenyl-oxy)-1,2,3,4-thiazotriazoles:



rapid isomerisation  $\rightarrow CH_2=CH-CH(R)-N=C=O$

The 2-alkenyl isocyanates were identified by comparison with authentic material, the formation of which, from "crotyl bromide" and silver cyanate, we wish to report here.

Although 2-butenyl bromide and 1-methylallyl bromide may both be obtained in a pure state, they are converted into an equilibrium mixture on standing at room temperature; thus the compound "crotyl bromide" is reported to consist of approximately 85% 2-butenyl bromide in equilibrium with 15% 1-methylallyl bromide.<sup>2,3</sup>

In our experiments "crotyl bromide" and silver cyanate in diethylether gave a mixture of the two possible isocyanates in 84% yield. <sup>1</sup>H NMR spectroscopy proved it to comprise 70% 2-butenyl isocyanate and 30% 1-methylallyl isocyanate. The isocyanates were separated by preparative GLC and identified by elemental analysis and by IR and <sup>1</sup>H NMR spectroscopy.

It has been demonstrated that the cyanate ion is ambident,<sup>4</sup> and it may therefore be assumed that some 2-butenyl and 1-methylallyl cyanate should be formed in the reaction between "crotyl bromide" and silver cyanate; however neither of these products has been observed. So far, this