Fig. 2. Conversion of all-*trans* (————) and 13-*cis* (— — — —) vitamin A_1 into anhydro vitamin A_1 in anhydrous 0.20 N ethanolic hydrogen chloride. The graph represents $E_{390}/E°_{max}$. plotted against time.

trans and 13-*cis* vitamin A_1 in 0.20 N ethanolic hydrochloric acid, and both magnitudes were found to be independent of $E°_{max}$. in a concentration range corresponding to $E°_{max}. = 0.1 - 1$.

Fig. 2 illustrates the difference in the dehydration reactions in the case of all-*trans* vitamin A_1 and 13-*cis* vitamin A_1, respectively, in 0.20 N ethanolic hydrochloric acid. It must be considered probable that the magnitudes $t_{max. anh.}$ and the maximum values of $E_{390} / E°_{max}$. for the different vitamin A_1 isomers will depend on the number of *cis* configurations and their positions in the molecule and on the molar extinction-coefficient of the vitamin A_1 isomer concerned.

An example of the application of the identification test described in the above will be published elsewhere [11].

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Depolymerization of 1,2-Dithiolane and 1,2-Diselenolane Polymers

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On hydrolysing trimethylendiselenocyanate, according to Hagelberg [1], Morgan and Burstall [2] a yellow powder is formed which was regarded as the monomer of 1,2-diselenolane (1,2-diselena-*cyclo*pentane) by Morgan and Burstall. Since this molecule is of great interest in connection with the spectrochemical investigations of diselenides, which are in progress at this institute by one of us [3], we tried to dissolve it in the common spectroscopic solvents. It was, however, found to be quite insoluble at ordinary temperatures, but when heated to about 60° the yellow powder darkened and went into solution. This solution was yellow and showed an absorption maximum at about 4 500 Å (Fig. 1). The colour persisted for several days at room temperature and then the yellow powder slowly precipitated. These facts indicate that the solution contains the monomer and that the yellow powder is a polymer, which depolymerizes when heated.

The corresponding sulphur compound (m. p. *ca.* 73°) prepared from trimethylendibromide and sodium disulphide [4] was also investigated. It dissolved without
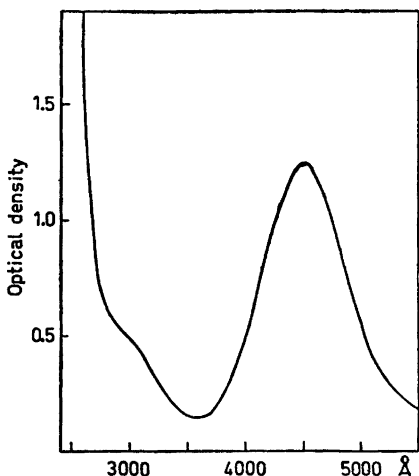
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Fig. 1. UV-absorption of 1,2-diselenolane in nujol.

colour change in hot lowboiling solvents and precipitated on cooling. On treating the above mentioned sulphur compound with paraffin oil or nujol a yellow solution was obtained at about 160°. The U.V.-absorption of the cooled, still yellow solu-
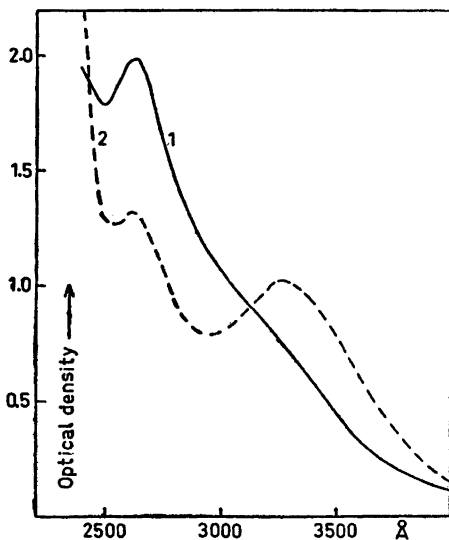

Fig. 2. Curve 1: UV-absorption of 1,2-dithiolane and polymer in nujol. Curve 2: UV-absorption of vapors collected in ethanol.

tion was recorded. It showed a peak at 2 630 Å and a weak shoulder at about 3 300 Å (Fig. 2). The peak comes from the normal absorption of linear disulphide and the shoulder indicates the presence of the 1,2-dithiolane. To confirm the presence of the characteristic 1,2-dithiolane peak (3 300 Å), we heated the solution and collected the vapors in ethanol. The U.V.-spectrum of the ethanol solution showed two distinct peaks; one from the polymer (2 620 Å) and one from the monomer (3 270 Å). The small shifts from the normal values of λ_{max} are in the expected directions for an absorption curve composed of two functions D_1 (λ) and D_2 (λ).

To complete our investigation of the depolymerization we determined the molecular weights by the Rast camphor-method. The molecular weight of the selenium compound was found to be 240 (calc. 200). This high value is in agreement with the shoulder in the spectrum (Fig. 1), indicating the presence of small amounts of polymer. Morgan and Burstall[2] found the molecular weight 225 in benzene. This misled them to believe that the substance was a monomer also in solid state.

No boiling point elevation could be detected, when an attempt was made to determine the molecular weight of the sulphur compound in benzene. This is in agreement with our assumption that the substance is dissolved as a polymer in lowerboiling solvents. The compound has earlier been considered as a dimer[5]. In molten camphor, however, it should be expected to be partly depolymerized. This was also found. The molecular weight depended on the time which the sample was in molten state. A rapid determination gave the molecular weight 740. After 3 h at 180° the mol.wt. was 205.

A similar depolymerization method for thioctic acid has recently been reported by Thomas and Reed[6].

The very easy depolymerization of the selenium compound as compared with the sulphur compound is remarkable.

The investigations on cyclic disulphides and diselenides are being continued.

Experimental. The spectra were determined with a Beckman model DU (2 450—4 000 Å) and a Beckman model B (4 000—5 500 Å) photoelectric spectrophotometer.

The molecular weights were determined in a Kofler hot-stage microscope.

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Eine verbesserte Methode zur Synthese neuer Nitrophenylester

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Ester des *p*-Nitrophenols wurden mit folgenden Säuren hergestellt: Essigsäure, Propionsäure, *Iso*buttersäure, Buttersäure, *Iso*valeriansäure, *n*-Valeriansäure, Capronsäure, Laurinsäure, Myristinsäure, Stearinsäure und Ölsäure.

Ein Teil dieser Ester war bereits von Huggins und Lapides [1] hergestellt worden, doch waren die flüssigen Produkte nicht durch ihre Siedepunkte charakterisiert worden. Für diese Ester und die vom Verfasser erstmalig hergestellten Ester sind Schmelz- und Siedepunkte in der Tabelle 1 angegeben.

Für die Synthese der Ester wurde die Methode von Spasov [2] abgeändert, da es sich erwies, dass die Wirkung des Magnesiums bei der Veresterung katalytisch und nicht stöchiometrisch ist. Daher wurde statt eines Äquivalents Magnesium (1/2 Mol) bloss 10 % der theoretischen Menge (1/20 Mol) verwendet. Um die Reaktion in Gang zu setzen wurde die Lösung mit einigen Körnchen Jod versetzt.

Durchführung der Synthesen. Zur Herstellung der niederen Fettsäureester bis inkl. der *Iso*buttersäure werden 13,9 g *p*-Nitrophenol, 0,12 Mol Säurechlorid, 0,12 g Magnesiumspäne, 30 g Benzol und einige Körnchen Jod eine Stunde, zur Herstellung der höheren Fettsäureestern vier Stunden unter Rückflusskühlung gekocht. Nach dem Abkühlen setzt man 150 ml Äthyläther, bei Myristinsäure- und Stearinsäureestern jedoch 150 ml Chloroform zu. Die Lösung wird darauf einmal mit 100 ml Wasser, zweimal mit 100 ml gesättigter Natriumbikarbonatlösung und schliesslich zweimal mit dest. Wasser gewaschen. Die nichtwässrige Schicht wird dann mit wasserfreiem Natriumsulfat getrocknet und mit Tierkohle behandelt. Nach dem Filtrieren wird die Lösung unter vermindertem Druck eingedampft. Die höheren

Tabelle 1.

p-Nitrophenyl ester der	Schmp. °C	Siedepunkt		Ausbeute %	*p*-Nitrophenolgehalt nach erfolgter Hydrolyse %	
		°C	Torr		Ber.	Gef.
*Iso*buttersäure	36,5—37					
n-Buttersäure	12—14	162—164	7	92		
*Iso*valeriansäure		158—160	6	86		
n-Valeriansäure		155—156	3	88	62,35	62,3
n-Capronsäure		174—175	6	84	58,8	61,8—63
Laurinsäure	44,5—45			79	43,36	43,5
Myristinsäure	54,5—55			85	39,85	39,9
Stearinsäure	66,5—67			86	34,34	34,4
Ölsäure		194—198	3	50		