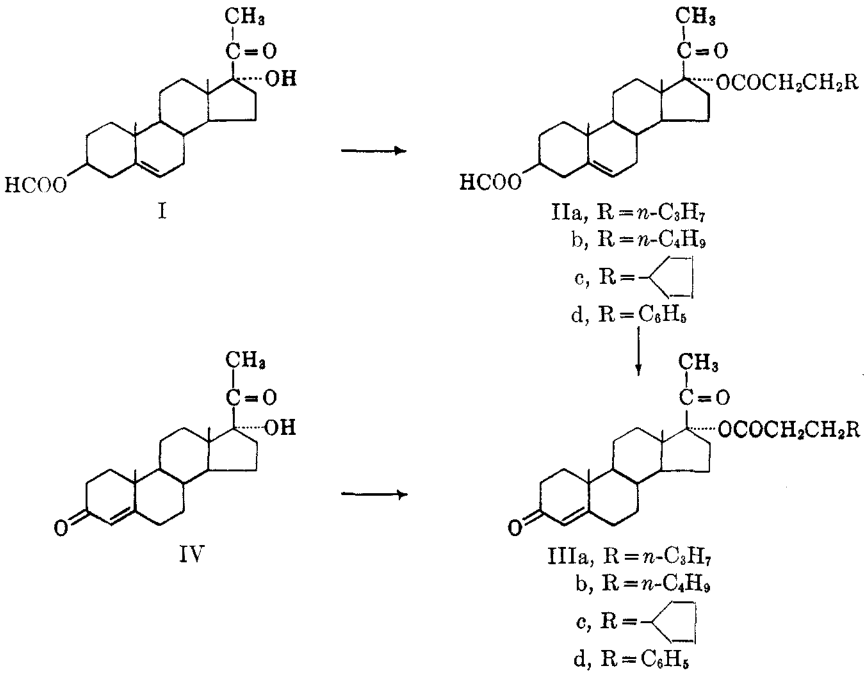

I

IIa, R = n-C_3H_7
b, R = n-C_4H_9
c, R =
d, R = C_6H_5

IV

IIIa, R = n-C_3H_7
b, R = n-C_4H_9
c, R =
d, R = C_6H_5

auer oxidation of IIa. Aluminum isopropoxide (3 g.) was added to a solution of 3 g. of the caproate IIa in 80 cc. of dry xylene and 30 cc. of dry cyclohexanone and the mixture was boiled under reflux for 45 minutes. Ice and water were added to the cooled reaction mixture which then was distilled in steam to effect removal of the solvents. The resulting solid was collected on Celite and dried. The product was extracted with acetone and was most efficiently purified by chromatography on 100 g. of neutral alumina. The fractions eluted with hexane–benzene (2:3 and 1:4) on crystallization from ether–hexane furnished 1.82 g. (65%) of 17α-hydroxyprogesterone n-caproate with m.p. 118–121°. The analytical sample showed m.p. 122–123°, $[\alpha]_D$ +57°, λ_{max} 240 mμ, log ϵ 4.23; reported:[2a] m.p. 120–121°.

Anal. Calc'd for $C_{27}H_{40}O_4$: C, 75.66; H, 9.41. Found: C, 75.72; H, 9.18.

(*b*) *By esterification of 17α-hydroxyprogesterone* (IV). A mixture of 3 g. of 17α-hydroxyprogesterone (IV), 4.5 g. of n-caproic anhydride, 0.6 g. of p-toluenesulfonic acid hydrate, and 100 cc. of dry benzene was heated at 80° until a clear solution was obtained (*ca.* 15 minutes). The solution then was allowed to stand at room temperature for 48 hours and the product was isolated as described above for the preparation of the caproate IIa. Chromatography on alumina and crystallization from ether–hexane produced 2.22 g. (57%) of the caproate IIIa with m.p. 118–120°, $[\alpha]_D$ +58°. The m.p. was undepressed on admixture with a sample prepared by method *a*.

17α-Hydroxyprogesterone enanthate (IIIb). (*a*) *From Δ⁵-pregnene-3β,17α-diol-20-one 3-formate* (I). The formate I was converted to the 3-formate 17-enanthate IIb in 74% yield as described above for the corresponding 17-caproate IIa, enanthic anhydride being substituted for caproic anhydride. The analytical specimen of IIb exhibited m.p. 90–91°, $[\alpha]_D$ −63°.

Anal. Calc'd for $C_{29}H_{44}O_5$: C, 73.69; H, 9.38. Found: C, 73.64; H, 9.29.

Oppenauer oxidation of the mixed diester IIb was carried out as with IIa and resulted in a 62% yield of 17α-hydroxyprogesterone enanthate with m.p. 113–114°, $[\alpha]_D$ +53°, λ_{max} 240 mμ, log ϵ 4.24; reported:[2a] m.p. 114–115°.

Anal. Calc'd for $C_{28}H_{42}O_4$: C, 75.97; H, 9.57. Found: C, 75.65; H, 9.69.

(*b*) *From 17α-hydroxyprogesterone* (IV). The esterification of 17α-hydroxyprogesterone with enanthic anhydride was performed as described above for caproic anhydride. The resulting enanthate IIIb (56% yield) showed m.p. 110–113°, $[\alpha]_D$ +52°. The m.p. was undepressed on admixture with a specimen prepared by method *a*.

17α-Hydroxyprogesterone cyclopentylpropionate (IIIc). This ester was prepared both from Δ^5-pregnene-3β,17α-diol-20-one 3-formate (I) and from 17α-hydroxyprogesterone (IV) as described above for the caproate IIIb and enanthate IIIc, cyclopentylpropionic anhydride being employed. 17α-Hydroxyprogesterone cyclopentylpropionate was crystallized from ether–hexane and showed m.p. 129–130°, $[\alpha]_D$ +47°, λ_{max} 240 mμ, log ϵ 4.23.

Anal. Calc'd for $C_{29}H_{42}O_4$: C, 76.61; H, 9.31. Found: C, 76.91; H, 9.38.

17α-Hydroxyprogesterone phenylpropionate (IIId). This ester was prepared both from I and IV as described for the other esters, phenylpropionic anhydride being used. It was crystallized from acetone–ether and exhibited m.p. 151–152°, $[\alpha]_D$ +64°.

Anal. Calc'd for $C_{30}H_{38}O_4$: C, 77.89; H, 8.28. Found: C, 77.91; H, 9.26.

SYNTEX, S. A.
APARTADO POSTAL 2679
MEXICO D. F.
MEXICO

Ultraviolet Absorption Spectra of Some Alkyl Disulfides and Methyl Trisulfide

GEORGE GORIN[1] AND GREGG DOUGHERTY

Received October 5, 1955

The ultraviolet absorption spectra of the normal alkyl disulfides from methyl through butyl and of methyl trisulfide have been measured in the range 220–320 mμ.

The spectra of ethyl, propyl, and butyl disulfides

---

(1) Thiokol Corporation Fellow, 1946–1948.

TABLE I

PHYSICAL PROPERTIES OF ALKYL POLYSULFIDES

	Boiling Point			Wave Length in mμ of		Extinction at
Compound	°C.	Mm.	n_D^{30}	Min.	Max.	Max.
Me_2S_2	107.2		1.5208	229	255	361
Et_2S_2	152		1.5021	227	250	430
Pr_2S_2	69–70	10	1.4940	227	251	425
Bu_2S_2	100.5–101.5	10	1.4891	227	251.5	422
Me_2S_3	58.4–59	15	1.5972			

are nearly identical. The position of and extinction coefficient at the inflection points are listed in Table I. The positions of the inflections for ethyl disulfide accord well with those reported by Mohler and Sorge,[2] although our extinction coefficients are appreciably different. In methyl disulfide, the maximum is shifted toward longer wave lengths and the absorption is somewhat lower. Figure 1 reports the spectrum of propyl disulfide, which is typical.

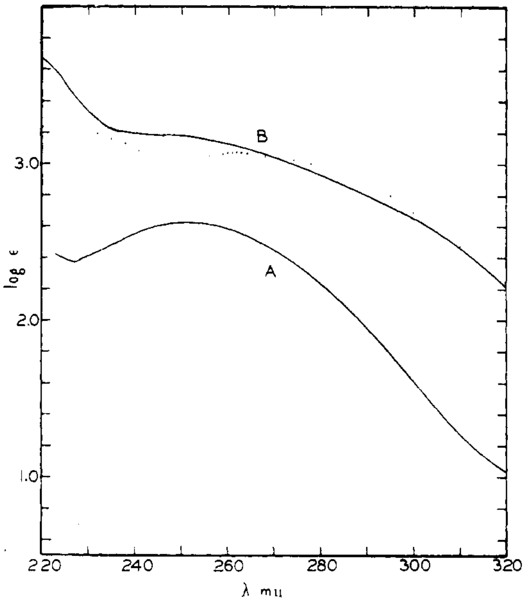

FIG. 1. ULTRAVIOLET ABSORPTION SPECTRA OF ALKYL POLYSULFIDES. A (————), propyl disulfide; B (————), methyl trisulfide and (•••••), mixture of methyl disulfide-sulfur (one mole: one gram-atom).

The spectrum of methyl trisulfide is also shown in Figure 1. Comparison with the curve found for *n*-hexadecyl trisulfide by Baer and Carmack[3] shows no greater differences than we have noted between methyl and the other disulfides. Therefore, the two trisulfides appear to be analogous. Recent evidence agrees to the point that isomerism is not found in tri-[4] and tetra- sulfides[5] prepared by different methods. The homogeneity of the sample used in this work was checked by repeated distillation; the spectrum reported did not change appreciably upon further fractionation.

It is noteworthy that the spectrum of methyl trisulfide differs quite markedly from that of a 1:1 mixture of methyl disulfide and sulfur (one mole: one gram-atom).

EXPERIMENTAL

Method and apparatus. All measurements were made with a Beckman quartz spectrophotometer, Model DU, the wave-length scale of which had been calibrated against the spectrum of a purified sample of benzene. Fused silica 1-cm. cells were employed; the slit width was varied as needed.

Approximately 0.05 *M* solutions were prepared by weighing appropriate amounts of the substances into volumetric flasks; lower concentrations were obtained by dilution. The solution of methyl disulfide and sulfur was 0.05/8 *M* in the latter (S_8) and the extinction coefficient was calculated by dividing by the concentration of either component.

Materials. The solvent used was a ligroin preparation purified according to Weissberger's directions[6] and consisting mainly of hexane.

The disulfides were Eastman Kodak "white label" products, with the exception of butyl disulfide; all were redistilled twice. Methyl trisulfide was prepared by the reaction of two moles of methyl sulfate with one mole of sodium sulfide and two gram-atoms of sulfur,[7] and was distilled three times. In every case the last distillation did not effect significant changes in the absorption spectrum. Pertinent physical properties are included in Table I.

The sulfur was prepared from a commercial product by double crystallization from 95% alcohol.

Acknowledgment. The authors wish to express their appreciation to Dr. F. O. Davis and Mr. E. M. Fettes of the Thiokol Corporation for their assistance and advice.

FRICK CHEMICAL LABORATORY
PRINCETON UNIVERSITY
PRINCETON, N. J.

---

(2) Mohler and Sorge, *Helv. Chim. Acta*, **23**, 1200 (1940).

(3) Baer and Carmack, *J. Am. Chem. Soc.*, **71**, 1215 (1949).

(4) Westlake, Laquer, and Smyth, *J. Am. Chem. Soc.*, **72**, 436 (1950).

(5) Koch, *J. Chem. Soc.*, 394 (1949).

(6) Weissberger, *Physical Methods of Organic Chemistry*, Interscience Publishers, New York, N. Y., 1946, p. 767.

(7) Stecker, *Ber.*, **41**, 1105 (1908).