4% aqueous sulfuric acid at room temperature for 20 min. The mixture was cooled to 0° and the crystalline glycol hydrates were collected on a filter, dissolved in ethyl ether, and the solution dried over anhydrous sodium sulfate. The ether was removed at reduced pressure, and the residue dissolved in benzene–petroleum ether and seeded with a crystal of the known diol (VII). Crystallization was allowed to proceed for 24 hr. at room temperature. This gave 0.870 g. (28%) of large colorless prisms, m.p. 69–71.4°. A recrystallized sample melted at 70–71.6° and had an infrared absorption curve identical in all respects with that of an authentic sample of diol VII. The filtrate from the 0.870 g. gave a mixture of diols (VII in prisms and VI in needles), 0.60 g., m.p. 48–68°.

The aqueous filtrate from the glycol hydrates was made weakly basic with aqueous sodium bicarbonate solution and extracted three times with ethyl ether. The combined extracts were dried over anhydrous sodium sulfate and the ether removed under vacuum. The residue was dissolved in petroleum ether (b.p. 30–60°) and crystallized at 40°. Long colorless needles, m.p. 55–61°, separated from the solution. Several crystallizations afforded 0.230 g. (7.4%) of diol VI melting at 65–66° which was further purified by vacuum sublimation. A mixture melting point of this diol with VII was 40–48°. The yield of VI obtained using this procedure is not representative of the amount actually present. These losses were necessary in order to obtain a sample free of the more insoluble diol (VII). The specific rotation of VI was $[\alpha]^{25}D$ +28 (10% acetone solution).

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.52; H, 10.64.

The infrared absorption maxima of VI and VII are compared: λ_{max}^{KBr} (VI) 2.97, 3.38, 6.05, 6.85, 7.23, 8.74, 9.26, 11.30 μ; (VII) 2.93, 3.38, 6.04, 6.83, 7.23, 8.40, 9.48, 9.68, 11.29 μ.

One milliliter (0.926 g.) of the *trans* epoxide (V) was shaken for 15 min. at room temperature with 15 ml. of 4% sulfuric acid.

The glycol hydrate which formed was collected on a filter, dissolved in ether, and the ether layer dried over anhydrous sodium sulfate. Removal of the ether at reduced pressure afforded 0.677 g. (66%) of colorless prisms, m.p. 66–69°. One recrystallization from benzene–petroleum ether solution gave 0.537 g. melting at 70–71.4° which proved to be identical in all respects to the known *trans* diol (VII). The yield and high degree of purity of VII obtained directly from the ether residue indicate that it is the main product. None of the more soluble diol (VI) could be recovered from the filtrates.

2-Amino-$\Delta^{8(9)}$-*p*-menthen-1-ol.—A 300-ml. capacity autoclave (Autoclave Engineers, Inc., Model No. ABA-300) was charged with 64 ml. (59.4 g.) of $\Delta^{8(9)}$-*p*-menthene 1,2-epoxide (I) and 100 ml. of aqueous ammonium hydroxide (28%). The mixture was stirred and heated at 135–140° for 4 hr. The crude product was then concentrated to dryness under vacuum using a film evaporator (water bath temp. 40°) and the residual dark viscous oil was vacuum distilled. At 95–99° (1.2 mm.), 49.0 g. (75%) of the mixed *trans* isomers of 2-amino-$\Delta^{8(9)}$-*p*-menthen-1-ol distilled as a colorless viscous oil. Redistillation afforded material boiling at 96–99° (1.2 mm.), d^{23} 0.9868, $n^{23}D$ 1.5032, $[\alpha]^{23}D$ +28.5.

Anal. Calcd. for $C_{10}H_{19}ON$: C, 70.96; H, 11.31; N, 8.28. Found: C, 71.25; H, 11.21; N, 8.26.

2-Methylamino-$\Delta^{8(9)}$-*p*-menthen-1-ol.—Sixty-four milliliters (59.4 g.) of $\Delta^{8(9)}$-*p*-menthene 1,2-epoxide (I) and 100 ml. of aqueous methylamine (30%) were stirred and heated at 135–140° in an autoclave for 5 hr. Concentration of the crude product to dryness gave a viscous oil which was vacuum distilled. At 89–94° (1.2 mm.), 46.7 g. (65%) of the mixed *trans* isomers of 2-methylamino-$\Delta^{8(9)}$-*p*-menthen-1-ol distilled as a colorless viscous oil. Redistillation afforded material boiling at 93–96° (1.3 mm.), d^{23} 0.9703, $n^{23}D$ 1.4964, $[\alpha]^{23}D$ +30.3.

Anal. Calcd. for $C_{11}H_{21}ON$: C, 72.08; H, 11.55; N, 7.64. Found: C, 71.84; H, 11.43; N, 7.68.

# Synthesis of β-Carotene and Certain Polyenes *via* Thiapyran Intermediates

ALBERT J. CHECHAK, MAX H. STERN, AND CHARLES D. ROBESON

β-Carotene has been synthesized by treating retinal with hydrogen sulfide and desulfurizing the new thio derivative thus formed, with metals in a basic solvent. The intermediate sulfur derivative of retinal has been assigned a 2,4-disubstituted 2*H* thiapyran structure (IIIa, R = B). Desulfurization of this thiapyran with amalgamated zinc in pyridine gave a good yield of β-carotene (70% over-all from retinal). Other β-methyl substituted conjugated aldehydes, such as β-ionylidene acetaldehyde, likewise gave 2,4-disubstituted thiapyrans and were desulfurized to polyenes.

The reaction of aromatic aldehydes with hydrogen sulfide to form trimeric thioaldehydes which can be desulfurized to ethylenic hydrocarbons is known. The reactions are illustrated by the conversion of trithiobenzaldehyde I to stilbene.[1]

I, R = C_6H_5
Ia, R = A

A
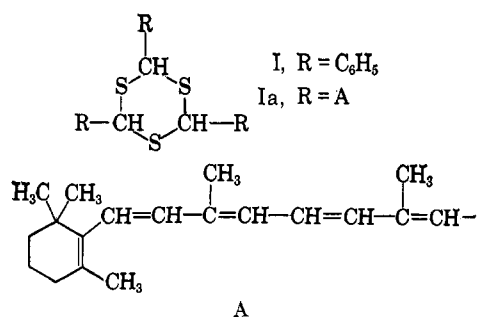
An attempt to prepare β-carotene in good yield from trithioretinal was, however, unsuccessful. Reaction of all *trans*-retinal with hydrogen sulfide, in ethanol, under conditions similar to those previously employed to prepare trimers[2] gave a compound Ia having properties consistent with I. This gave less than a 4% yield of β-carotene by the usual desulfurization procedures[1].

However, when hydrogen sulfide reacted with either all *trans*-retinal or 13-*cis*-retinal at low temperatures in amine solvents (*e.g.*, aniline, pyridine, etc.) a different type of sulfur containing intermediate was formed. Studies provided evidence that this intermediate had the thiapyran structure IIIa (R = B). We consider a 1,6-addition of hydrogen sulfide to retinal followed by ring closure to be a plausible mechanism for the forma-

III

IIIa, R=B
IIIb, R=C

B

C
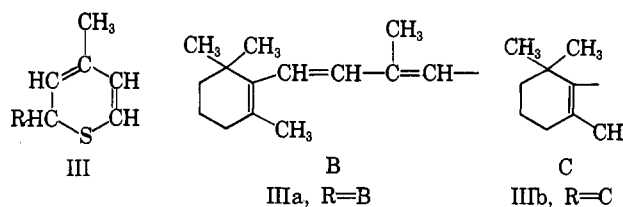
(1) E. Campaigne, *Chem. Rev.*, **39**, 52 (1946).

(2) E. Campaigne, *ibid.*, **39**, 4, 11 (1946).

TABLE I

SPECTRAL PROPERTIES OF THIAPYRAN INTERMEDIATES, III, AND POLYENE ALDEHYDE PRECURSORS, II

R		Ultraviolet absorption λ_{max}	ϵ	Infrared absorption λ_{max} (trans CH=CH)	K	λ_{max} (cis CH=CH)	K
B	Aldehyde	380	43,400	10.36	1.2	No peak	
	Thiapyran	274	16,650	10.28	0.52	14.2	0.38
$C_6H_5CH=CH-$	Aldehyde	351	32,500	10.17	1.3	No peak	
	Thiapyran	260	20,100	10.42	0.78	14.3	0.64
C_6H_5-	Aldehyde	322	25,800	10.42	0.56	No peak	
	Thiapyran	End absorption		No peak		14.3	0.90
C	Aldehyde	326	15,600	10.31	0.75	No peak	
	Thiapyran	End absorption		No peak		14.3	0.60

tion of a thiapyran. The compound readily desulfurized to β-carotene in good yield when heated with amalgamated zinc in pyridine solution. Evidence was obtained that the desulfurization reaction proceeds

$$R-CH=CH-\underset{\underset{II}{\overset{\overset{CH_3}{|}}{C}}}{=}CH-CHO \xrightarrow[\text{solvent}]{\overset{H_2S}{\underset{amine}{}}}$$
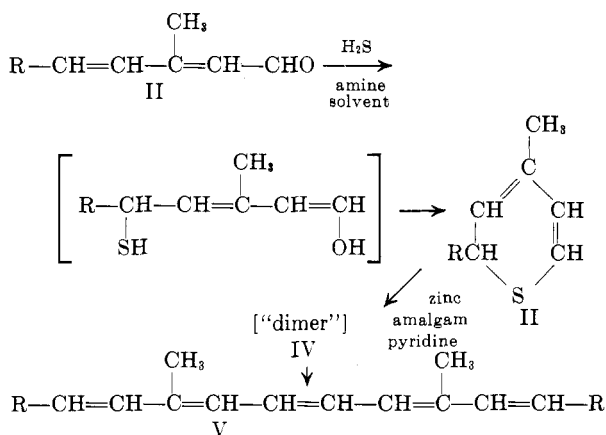
via an intermediate dimer IV, probably a substituted 1,2- or 1,3-dithietane.

Thiapyran Formation.—The 1,6-addition of thiols to unsaturated steroidal ketones has been described.[3,4] However, no reports have been found which describe either the preparation of 2,4-dialkyl substituted thiapyrans or 1,6-addition of hydrogen sulfide to conjugated aldehydes.

Factors influencing the formation of thiapyrans from conjugately unsaturated aldehydes were hence investigated. A methyl substituent on the carbon atom β to the aldehyde group, as in retinal, appeared to be one requirement. For example, we were unable to prepare thiapyrans from 13-desmethylretinal or from 7-phenyl-heptatrienal.

Stereochemical configuration is a second factor influencing the formation of thiapyrans. When hydrogen sulfide reacted with 13-cis-retinal, under our preferred conditions, (in pyridine, $-10°$) a 95% yield of thiapyran IIIa was obtained. The corresponding yield from all trans-retinal was only 50%. It appears that the cis configuration either favors 1,6-addition of hydrogen sulfide to the aldehyde or leads to an intermediate which forms the thiapyran ring more readily.

The yield from the trans isomer was improved by the addition of certain amine hydrochlorides. Thus, it was found that by incorporating a small amount of aniline hydrochloride in the reaction, the yield of thiapyran from the all trans isomer was increased to that

obtained from the 13-cis isomer. Although no cis isomer could be detected when all trans-retinal in cold pyridine or aniline was treated with aniline hydrochloride, in the absence of hydrogen sulfide, this does not exclude the possibility of a trans-to-cis conversion in the presence of hydrogen sulfide.

A 2,4-disubstituted 2H thiapyran structure (IIIa, R = B) is proposed for the thiointermediate from the following evidence: (1) molecular weight determination and elemental analysis indicated it to be a monomeric derivative of retinal in which oxygen had been replaced by sulfur; (2) the infrared absorption spectrum showed that the absorption band at 6.01 μ, characteristic of the carbonyl group in the original aldehyde, was no longer present; (3) the intensity of absorption at 10.28 μ for the thiapyran corresponded approximately to the loss of one of the two nonmethyl substituted trans double bonds in retinal; (4) the ultraviolet absorption spectrum showed a maximum at 274 mμ characteristic of a conjugated triene.

Thiapyrans were prepared from other β-methyl-polyene aldehydes. Their infrared and ultraviolet absorption properties (Table I) were likewise consistent with a III-type structure.

For example, the intensity of the trans CH=CH band at 10.4 μ in the infrared spectrum of the product from 7-phenyl-3-methylheptatrienal, as in the case of retinal, corresponded approximately to the loss of one of the two such groups present in the parent aldehyde. In the case of β-ionylidene acetaldehyde (II, R = C) and 5-phenyl-3-methylpentadienal (R = C_6H_5) which have only one trans CH=CH bond, the 10.4-μ band was not present in the spectra of the thio derivatives. A band at 14.2–14.3 μ in the infrared spectra of all these compounds, not present in the spectra of the precursor aldehydes, may be characteristic of the cis double bond of the heterocyclic ring. Disubstituted cis ethylenic centers are known to absorb in this region of the spectrum.[5]

In the case of each of these aldehydes, the ultraviolet absorption maximum of the corresponding derivative is at a wave length consistent with the new shorter chromophore in the proposed formula for the thio derivative.

Desulfurization.—Evidence for the formation of the intermediate (IV) in the desulfurization reaction came from the ultraviolet spectra of aliquots of the reaction mixture taken at intervals (Fig. 1). After heating a pyridine solution of thiapyran IIIa (R = B), λ_{max} 274 mμ, for 2 hr. in the presence of zinc amalgam, the absorption maximum was shifted to 335 mμ accompanied
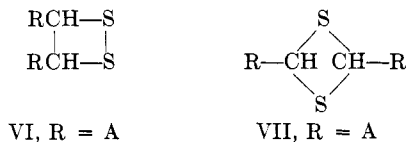
(3) J. W. Ralls, R. M. Dodson, and B. Riegel, *J. Am. Chem. Soc.*, **71**, 3320 (1949).

(4) J. Romo, G. Rosenkranz, and C. Djerassi, *J. Org. Chem.*, **17**, 1413 (1952).

(5) H. Henbest, G. Meakins, and G. Wood, *J. Chem. Soc.*, 800 (1954).

by a small build-up of extinction in the 450-mμ region due to β-carotene. After 8 hr., substantial amounts of β-carotene had formed and the absorption at 335 mμ was reduced.

The properties of a purified sample of IV were consistent with dithietane structures VI or VII (R = A).

$$\begin{array}{cc} \text{RCH—S} & \text{S} \\ \text{RCH—S} & \text{R—CH CH—R} \\ & \text{S} \\ \text{VI, R = A} & \text{VII, R = A} \end{array}$$

Molecular weight determination and elemental sulfur analysis indicated it to be a dimer. From its ultraviolet absorption maximum, which is at the same wave length (335 mμ) as that of trithiane Ia (R = A), and from its infrared absorption spectrum, (no hydroxyl or carbonyl band, strong 10.3-μ band (trans CH=CH), no 14.3-μ band), either of the proposed dithietane structures are reasonable. The instability of the compound, evidenced by a tendency to decompose to polymeric tars on storage and its ready desulfurization to β-carotene favors the 1,2-dithietane structure (VI). Cyclic 1,2-disulfides are known to be unstable[6] and a 1,3-dithietane structure has been proposed[7] for one highly stable fluorocarbon heterocyclic compound.

Optimum yields (ca. 70%) of β-carotene were obtained by heating pyridine or quinoline solutions of the thiapyran III for a period of 5 to 10 hr. at 70°, in the presence of zinc amalgam, prepared according to Martin.[8] Lower yields were obtained when the metal was omitted or when the reaction was run in other solvents including benzene, toluene, or triethylamine. A variety of metal catalysts including Raney nickel, palladium–calcium carbonate, precipitated copper, magnesium amalgam, lithium, phenyllithium, and others were tested and found to give lower yields of β-carotene than zinc amalgam.

Desulfurization of the other thiapyrans listed in Table I gave concentrates of polyene hydrocarbons with ultraviolet absorption spectra in the range expected for the compounds of the following structure.

$$\begin{array}{c} \text{CH}_3 \\ | \\ [\text{R—CH=CH—C—CH—CH=}]_2 \end{array}$$
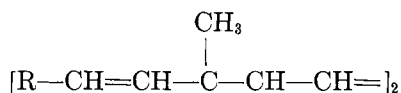
The pure hydrocarbons were not prepared.

Experimental

The ultraviolet and infrared spectrographic measurements were made by Mr. W. Blum of this laboratory using a Cary recording spectrophotometer, Model 11M, and a Perkin-Elmer spectrophotometer, Model 21, respectively. Ultraviolet spectra were determined in ethanol solution unless otherwise stated. Melting points were determined in capillary tubes, using 3-in. immersion thermometers. The microanalyses were done by the Microanalytical Laboratory of the Eastman Kodak Company under the direction of Mr. D. Ketchum. Molecular weight values were determined (benzene) using a Beckman molecular weight apparatus.[9]
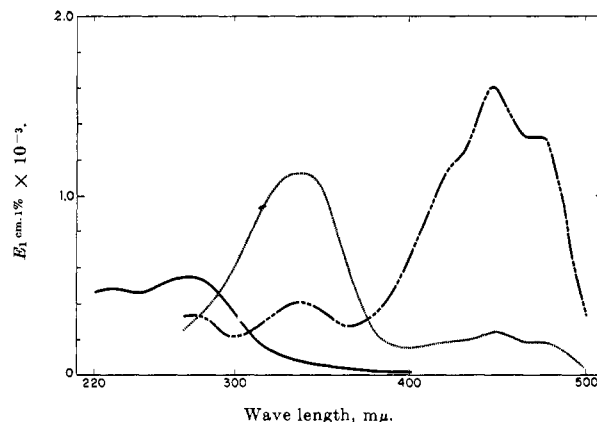
Fig. 1.—Change in ultraviolet and visible absorption spectrum during desulfurization: thiapyran, ———; after 2 hr., ᴵᴵᴵᴵᴵᴵᴵᴵᴵ; after 8 hr., - - ———.

Preparation of Trithioretinal (Ia, R = A).—Hydrogen sulfide gas was passed through a stirred solution of trans-retinal (14.2 g.) in 85% aqueous ethanol (142 ml.) at room temperature for 6 hr. The yellow-orange solids which separated were collected by filtration, dissolved in chloroform (100 cc.) and reprecipitated by adding the chloroform solution to 250 cc. of methanol. The bright yellow solids were collected, washed repeatedly with methanol, and dried under vacuum yielding 7.6 g. of product, ε (335 mμ) 107,200 (in petroleum ether, b.p. 60–71°); strong infrared absorption band at 10.3 (trans CH=CH), no band at 6.01 μ (carbonyl).

Anal. Calcd. for $C_{60}H_{84}S_3$: C, 79.9; H, 9.4; S, 10.7; mol. wt., 901. Found: C, 79.5; H, 9.8; S, 10.9; mol. wt., 927.

Desulfurization of Ia.—A portion (3.0 g.) of trithioretinal (Ia) was mixed with freshly precipitated copper (3.0 g.) prepared according to the method of Stanfield and Reynolds.[10] This mixture was stirred under an atmosphere of nitrogen while the temperature was gradually raised to 100° over a period of 0.5 hr. The reaction mixture was then cooled and extracted with benzene. Evaporation of the solvent gave a dark colored residue (2.97 g.) whose ultraviolet absorption spectrum showed E (1%, 1 cm., 290 mμ) 344. No absorption characteristic of β-carotene was evident.

Modification of these conditions in which solutions of the trithioretinal (1.0 g.) in benzene (6 ml.) were stirred with the copper at room temperature for 15 hr. or refluxed for periods up to 8 hr. likewise gave products with changed ultraviolet absorption spectra indicating that decomposition of the trithioretinal had occurred. From the absorption measured at 450 mμ, it was calculated that they contained, at most, 1.3% β-carotene.

Other attempts to desulfurize the trithioretinal included refluxing a xylene solution of the compound with Raney nickel and heating it in pyridine solution in the presence of amalgamated zinc. In every case the ultraviolet absorption spectra of aliquots showed that β-carotene was not formed in yields greater than 4% as estimated from the absorption at 450 mμ.

Preparation of Aldehydes (II).—The preparation of β-ionylidene acetaldehyde (II, R = C) and of retinal (II, R = B) has been previously reported.[11,12] (In the new nomenclature[13] for vitamin A isomers, 13-cis-retinal corresponds to 2-cis-vitamin A aldehyde of ref. 11.)

The II aldehydes (R = C₆H₅ and C₆H₅CH=CH—) were prepared from the corresponding 5-phenyl-3-methyl-2,4-pentadienoic and 7-phenyl-3-methyl-2,4,6-heptatrienoic acids[14] by the steps reported for the preparation of β-ionylidene acetaldehyde from β-ionylideneacetic acid.[11]

5-Phenyl-3-methyl-2,4-pentadienoic acid (10 g.) was converted to its methyl ester (10.6 g., ε (311 mμ) 29,000). The ester was dissolved in dry ethyl ether (175 ml.) and treated with lithium aluminum hydride (33 ml. of 1 M solution) for 3 min. at 5°.

(6) J. Affleck and G. Dougherty, J. Org. Chem., **15**, 865 (1950).

(7) M. Hauptschein and M. Braid, J. Am. Chem. Soc., **80**, 853 (1958).

(8) E. Martin, ibid., **58**, 1438 (1936).

(9) F. Daniels, J. H. Mathews, and J. W. Williams, "Experimental Physical Chemistry," 4th Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1949, pp. 84–86.

(10) J. Stanfield and L. Reynolds, J. Am. Chem. Soc., **74**, 2878 (1952).

(11) C. D. Robeson, J. D. Cawley, L. Weisler, M. H. Stern, C. C. Eddinger, and A. J. Chechak, ibid., **77**, 4111 (1955).

(12) C. D. Robeson, W. P. Blum, J. M. Dieterle, J. D. Cawley, and J. G. Baxter, ibid., **77**, 4120 (1955).

(13) Commission on the Nomenclature of Biological Chemistry, ibid., **82**, 5575 (1960).

(14) J. D. Cawley and D. R. Nelan, ibid., **77**, 4130 (1955).

The reaction mixture was hydrolyzed with dilute (5%) sulfuric acid. The ether solution was washed successively with dilute acid, 0.5 N potassium hydroxide, and water, dried over anhydrous sodium sulfate, and filtered. Evaporation of the solvent gave 8.8 g. of 5-phenyl-3-methyl-2,4-pentadien-1-ol which crystallized from ethanol at 5°, m.p. 68–69°; ϵ (280, 288 mμ) 27,650 and 29,300.

Anal. Calcd. for $C_{12}H_{14}O$: C, 82.7; H, 8.1. Found: C, 82.8; H, 8.1.

A solution of the alcohol (5.0 g.) in diethyl ether (75 ml.) was mixed with manganese ·dioxide powder[15] (75 g.) and allowed to stand at room temperature for 20 hr. After filtering and washing the filter cake thoroughly with ether, the filtrate and washings were evaporated to give a residue of yellow oil [E (1%, 1 cm., 322 mμ) 1450]. Crystallization from petroleum ether (b.p. 60–71°) at 20° gave pure II (R = C_6H_5), m.p. 25°; ϵ (239, 322 mμ) = 12,250 and 25,800.

Anal. Calcd. for $C_{12}H_{12}O$: C, 83.7; H, 7.0. Found: C, 83.3; H, 7.1.

7-Phenyl-3-methyl-2,4,6-heptatrienoic acid [6.8 g., ϵ (335 mμ) 40,800] was converted to its methyl ester [7.0 g., ϵ (337 mμ) 46,300]. The ester was dissolved in dry ethyl ether (100 ml.), treated with lithium aluminum hydride and worked up as described before for 5-phenyl-3-methyl-2,4-pentadien-1-ol to yield 6.1 g. of tan colored solids. Crystallization of the solids from aqueous ethanol at 5° gave 7-phenyl-3-methyl-2,4,6-heptatrien-1-ol as light yellow prisms, m.p. 75°; ϵ (304, 318, 333 mμ) 39,800, 49,800, 37,400.

Anal. Calcd. for $C_{14}H_{16}O$: C, 83.9; H, 8.0. Found: C, 83.7; H, 7.9.

A solution of the alcohol (3.0 g.) in ethyl ether was oxidized with manganese dioxide powder (45 g.) as described for II (R = C_6H_5). The product II (R = $C_6H_5CH=CH-$, 2.65 g.) consisted of a light yellow oil having E (1%, 1 cm., 261 and 351 mμ) 800 and 1735. Its infrared absorption spectrum showed a strong band at 6.01 (carbonyl) and no band at 2.76 μ (hydroxyl). It was not further purified.

Preparation of Thiapyrans (III).—The thiapyrans listed in Table I were made and purified by the general method illustrated by the following example for the thiapyran from 13-*cis*-retinal.

A solution of 13-*cis*-retinal (10.0 g.) in dry pyridine (15 ml.) was added dropwise to cold ($-10°$) pyridine (85 ml.), previously saturated with hydrogen sulfide gas. The reaction mixture was stirred at this temperature with continuous flow of a stream of hydrogen sulfide gas through the solution for 4 hr. The reaction mixture was then diluted with isopropyl ether (300 ml.) and the ether phase washed successively with two portions of cold dilute (5%) hydrochloric acid, once with saturated aqueous sodium bicarbonate solution, and finally with water until the washings were neutral. After drying over anhydrous sodium sulfate, the ether was evaporated, leaving a residue (10.4 g.) of red oil having E (1%, 1 cm., 274 mμ) 527.

This oil was dissolved in petroleum ether (b.p. 60–71°) and chromatographed on a column (6 cm. × 24 cm.) of magnesium silicate adsorbant (Florisil, 60–100 mesh, Floridin Co.). Continued washing of the column with petroleum ether gave a filtrate containing the nonadsorbed fraction which showed up as a greenish yellow zone on the column. Evaporation of the solvent from this fraction gave 8.0 g. of purified IIIa (R = B) as a pale yellow oil, ϵ (274 mμ) 16,650.

Anal. Calcd. for $C_{20}H_{28}S$: C, 79.9; H, 9.4; S, 10.7; mol. wt., 300. Found: C, 79.5; H, 9.4; S, 10.5; mol. wt., 325.

Similar results were obtained in experiments when other amines including quinoline, N-ethylaniline, or aniline were substituted for pyridine in the previous procedure.

Substitution of all *trans*-retinal for the 13-*cis* isomer in this procedure gave a compound having the same properties after the chromatographic purification as those for the product from the 13-*cis* isomer, but the yield was lower (estimated 50%). The remainder of the reaction product was judged to be mainly trithioretinal as indicated by ultraviolet and infrared absorption properties of the more strongly absorbed fractions. To obtain

high yields of III from the all *trans* isomer, it was necessary in the procedure described before to add the pyridine solution of retinal to cold aniline saturated with hydrogen sulfide and containing also approximately 0.4% aniline hydrochloride. The product, after purification by chromatography, had ϵ (274 mμ) 16,700.

Anal. Calcd. for $C_{20}H_{28}S$: C, 79.9; H, 9.4; S, 10.7; mol. wt., 300. Found: C, 79.6; H, 9.4; S, 10.7; mol. wt., 311.

For III (R = $C_6H_5CH=CH-$), there was obtained 1.56 g. from 2.0 g. of aldehyde.

Anal. Calcd. for $C_{14}H_{14}S$: C, 78.5; H, 6.6; S, 14.9; mol. wt., 214. Found: C, 78.8; H, 6.8; S, 14.8; mol. wt., 268.

For III (R = C_6H_5), there was obtained 0.72 g. from 1.5 g. of aldehyde.

Anal. Calcd. for $C_{12}H_{12}S$: C, 76.5; H, 6.5; S, 17.0; mol. wt., 188. Found: C, 77.3; H, 6.9; S, 17.2; mol. wt., 216.

For IIIb (R = C), there was obtained 2.6 g. from 5.95 g. of aldehyde.

Anal. Calcd. for $C_{15}H_{22}S$: C, 76.9; H, 9.4; S, 13.7; mol. wt., 234. Found: C, 76.9; H, 8.9; S, 13.7; mol. wt., 250.

Preparation of "Dimer" (IV).—A solution of IIIa (R = B, 8.0 g.) in pyridine (80 ml.) was added to freshly prepared amalgamated zinc (16 g.) and allowed to stand at room temperature overnight. The reaction mixture was filtered and the filter cake was washed with 200 ml. of diethyl ether. The filtrate and washings were combined, and the ether phase was washed several times with dilute (5%) hydrochloric acid, twice with saturated aqueous sodium bicarbonate solution, and finally with water until the washings were neutral. After drying over anhydrous sodium sulfate, the ether was evaporated leaving 8.2 g. of an orange solid. These were recrystallized from chloroform-methanol (1:1) to give yellow crystals having ϵ (335 mμ) 70,300. Its infrared absorption spectrum showed a strong band at 10.3 (-CH=CH-) and absence of bands at 14.25 and 6.01 μ.

Anal. Calcd. for $C_{40}H_{56}S_2$: C, 79.9; H, 9.4; S, 10.7; mol. wt., 600. Found: C, 80.0; H, 9.3; S, 11.1; mol. wt., 587.

Preparation of Polyenes (V).—Desulfurizations of the thiapyrans (III) were carried out by the general method illustrated by the following example for the preparation of β-carotene.

A solution of 9.9 g. of IIIa (R = B) in 100 ml. of dry pyridine was saturated with carbon dioxide by bubbling the gas through the solution for 15 min. It was then added to freshly prepared and pulverized amalgamated zinc (20 g.) and after 1 hr., the temperature was raised to 70° and the reaction held at this temperature for 9 hr. under an atmosphere of carbon dioxide. After cooling to 20°, the mixture was filtered and the filter cake washed throughly with isopropyl ether. The filtrate and ether washings were combined, and the ethereal phase was washed successively with 5% hydrochloric acid, saturated aqueous sodium bicarbonate solution, and water until washes were neutral. After drying over anhydrous sodium sulfate, the ether was distilled to yield 9.5 g. of a β-carotene concentrate as a red solid [E (1%, 1 cm., 450 mμ) 1580]. A sample was recrystallized twice from benzene–ethyl formate (1:1) at 0° to give pure all *trans*-β-carotene as violet plates having ϵ (432, 456, 485 mμ) 92,600, 135,300, 118,500 (cyclohexane). The crystals melted at 182–182.5°. The melting point, when mixed with a sample of authentic all *trans*-β-carotene, was undepressed.

The polyene product from IIIb (R = C) was an oil which had an ultraviolet absorption maximum at 369 mμ [E (1%, 1 cm.) 605] and was not further purified. A crystalline preparation made by a different method and having E (1%, 1 cm., 372 mμ) 1400 has been reported.[16]

The diphenyl polyene V (R = C_6H_5), was a yellow solid, E (1%, 1 cm., 390, 411, and 437 mμ) 1825, 2710, 2320 (in benzene). V (R = $C_6H_5CH=CH-$) was an orange solid, E (1%, 1 cm., 409, 433, and 462 mμ) 2630, 4090, 3800 (in petroleum ether, b.p. 60–71°). This was the expected range for the ultraviolet absorption of these polyenes based on values reported[17] for the corresponding diphenyl polyenes containing no branched methyl groups.

(15) "Precipitated" grade, General Metallic Oxides Co.

(16) H. Inhoffen, F. Bohlmann, H. Aldag, S. Bork, and G. Liebner, *Ann.* **573**, 1 (1951).

(17) K. Dimroth, *Angew. Chem.*, **52**, 545 (1939).