splitting of the $\nu_{COOH}$ band at 1735 $cm^{-1}$ ($\sim 15\ cm^{-1}$) is retained in the IR spectrum of the dehydrated product. Two intense absorption bands at 1625 and 1673 $cm^{-1}$ appear in the 1600-1700 $cm^{-1}$ region. The 1625 $cm^{-1}$ band most probably belongs to the betaine ion [3]. The absorption bands of water in the 3000-3600 $cm^{-1}$ region disappear on dehydration. The dehydration curve consists of two sections, which correspond to the successive removal of three and two molecules of water.

## CONCLUSIONS

1. The following complexes of Pd(II) with diethylenetriaminepentaacetic acid were synthesized for the first time: $H_3PdL\cdot 5H_2O$, and $H_4PdLX\cdot 3H_2O$, where X = Cl, Br.

2. From the IR spectra of the obtained compounds it follows that the carboxyl groups of diethylenetriaminepentaacetic acid are partially coordinated by palladium.

3. Employing thermographic analysis, it was ascertained that the water in the isolated halogen-containing complexes is very firmly bound and is not removed clear up to the decomposition temperature. Two types of hydrate water are present in $H_3PdL\cdot 5H_2O$.

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# DIRECTION OF EPOXIDATION OF ESTERS OF POLYUNSATURATED ACIDS

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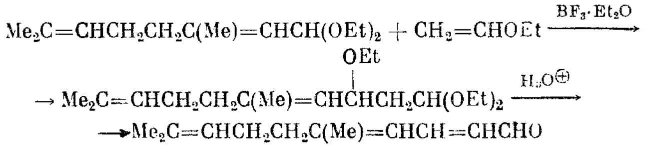
The synthesis of the esters of isoprenoid acids with epoxide rings is of interest from the standpoint of obtaining compounds with potential juvenile hormone activity. In the present paper we synthesized a number of such oxiranes by starting with the polyunsaturated esters (I), (II), and (III), which were obtained employing the Horner variation of the Wittig reaction [1]. Thus, the reaction of citral (based on the GLC data, a 3:2 mixture of the cis-trans isomers) and its vinylog with $(EtO)_2P(O)CHRCO_2Et$ (R = H, $C_6H_{13}$) gave (I), (II), and (III), in which connection we obtained $(EtO)_2P(O)CH(C_6H_{13})CO_2Et$ for the first time by the Arbuzov rearrangement from $C_6H_{13}CHBrCO_2Et$ and $(EtO)_3P$ in quite high yield. The citral vinylog was synthesized from citral diethyl acetal by adding vinyl ethyl ether to it, followed by acid hydrolysis of the formed triethoxy acetal by the scheme given in [2].



$$Me_2C{=}CHCH_2CH_2C(Me){=}CHCH(OEt)_2 + CH_2{=}CHOEt \xrightarrow{BF_3\cdot Et_2O}$$
$$\rightarrow Me_2C{=}CHCH_2CH_2C(Me){=}CH\overset{\overset{OEt}{|}}{C}HCH_2CH(OEt)_2 \xrightarrow{H_3O^{\oplus}}$$
$$\rightarrow Me_2C{=}CHCH_2CH_2C(Me){=}CHCH{=}CHCHO$$

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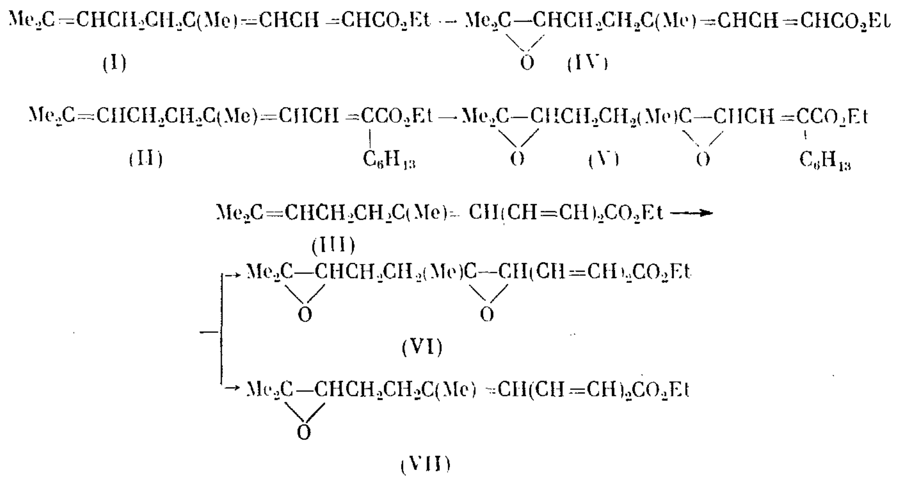
The reaction of diethyl carbethoxymethylphosphinate with citral and its vinylog is stereospecific and leads to the trans isomers at the generated double bond. The reaction of diethyl carbethoxyhexylmethylenephosphinate with citral leads to the formation of a mixture of the cis–trans isomers at the generated double bond, which is confirmed by the IR spectrum of ester (III).

The epoxidation of esters (I)-(III) was accomplished by treatment with perphthalic acid at the moment of its formation from phthalic anhydride and $H_2O_2$ in the presence of urea [3]. Under these conditions the oxidation of ester (I), as was to be expected, proceeds exclusively at the more electrophilic terminal double bond to give (IV).



$$\mathrm{Me_2C{=}CHCH_2CH_2C(Me){=}CHCH{=}CHCO_2Et} \rightarrow \mathrm{Me_2\underset{\diagdown O \diagup}{C{-}CH}CH_2CH_2C(Me){=}CHCH{=}CHCO_2Et}$$

(I) (IV)

$$\mathrm{Me_2C{=}CHCH_2CH_2C(Me){=}CHCH{=}\underset{C_6H_{13}}{C}CO_2Et} \rightarrow \mathrm{Me_2\underset{\diagdown O \diagup}{C{-}CH}CH_2CH_2\underset{\diagdown O \diagup}{(Me)C{-}CH}CH{=}\underset{C_6H_{13}}{C}CO_2Et}$$

(II) (V)

$$\mathrm{Me_2C{=}CHCH_2CH_2C(Me){=}CH(CH{=}CH)_2CO_2Et} \rightarrow$$

(III)

$$\rightarrow \mathrm{Me_2\underset{\diagdown O \diagup}{C{-}CH}CH_2CH_2\underset{\diagdown O \diagup}{(Me)C{-}CH}(CH{=}CH)_2CO_2Et}$$

(VI)

$$\rightarrow \mathrm{Me_2\underset{\diagdown O \diagup}{C{-}CH}CH_2CH_2C(Me){=}CH(CH{=}CH)_2CO_2Et}$$

(VII)

In ester (II) the shift of the π-electron density from the polyene chain to the ester group is compensated by the +I effect and the hyperconjugation effect of the alkyl substituent in the α position. This leads to the retention of a quite high electron density on the 3,4 double bond, and the oxidation of ester (II) becomes possible at the two double bonds furthest away from the carbethoxyl group to give dioxide (V). In ester (III) the presence of a longer polyene chain leads to a retention of the electrophilic character of the 5,6 double bond, and epoxidation in this case leads to dioxide (VI). However, when equimolar amounts of the reactants are used the oxidation of (III) proceeds with the formation of a mixture of dioxide (VI) and monooxide (VII) in an $\sim$3:2 ratio (judging by the NMR spectrum).

The structure of all of the obtained compounds was proved on the basis of the IR, UV, and NMR spectra (Table 1). The purity of the products was checked by TLC; the same method was used to check the reaction course.

## EXPERIMENTAL

The NMR spectra were taken on a Varian DA-60-IL instrument (60 MHz) in $CCl_4$ solution, using TMS as the internal standard, and the chemical shifts are given on the δ scale. The IR spectra were taken on a UR-20 instrument in $CHCl_3$ solution, and the UV spectra were taken on a Specord UV-VIS instrument in alcohol solution.

Diethyl Carbethoxyhexylmethylenephosphinate. To 49.8 g (0.3 mole) of triethyl phosphite, heated to 140-150°C, was added in drops 65.8 g (0.3 mole) of ethyl α-bromo-n-caprylate, with the simultaneous removal of the cleaved $C_2H_5Br$ by distillation. Then the mixture was heated at the same temperature for 5-6 h, after which it was fractionally distilled in vacuo. Yield 72%, bp 145-148° (0.4 mm), $n_D^{18}$ 1.4400.

Geranylacrylaldehyde. a) To 50 ml (0.3 mole) of citral were added 68.5 ml (0.33 mole) of tetraethoxysilane, 5.3 ml of alcohol, and several drops of 85% $H_3PO_4$. The mixture was let stand for three days at $\sim$20°, after which it was treated with 320 ml of 30% NaOH solution, and the upper layer was separated and dried over $K_2CO_3$. Fractional distillation gave citral diethyl acetal in 75% yield, bp 125-130° (20 mm).

b) To a mixture of 0.1 mole of citral diethyl acetal and 0.1 ml of $BF_3 \cdot Et_2O$ was added in drops 0.1 mole of vinyl ethyl ether in such manner that the temperature did not exceed

TABLE 1

| Compound | Yield, % | bp, °C (p, mm of Hg) | $n_D^{18}$ | NMR spectrum (δ, ppm), J, Hz | Infrared spectrum (ν, cm$^{-1}$) | Ultraviolet spectrum $\lambda_{max}$, nm (ε) |
|---|---|---|---|---|---|---|
| (I) | 67 | 85–90 (0,05) | 1,5082 | 1,23 t (3H, ester $CH_3$ $J=7$); 1,55–1,96 m (9H, $3CH_3$); 2,05–2,35 m (4H, $2CH_2$); 4,10 q (2H, $2CH_2$ of ester $J=7$); 5,00 m (1H, $(CH_3)_2C-C\underline{H}-$); 5,75 d (1H, $=C\underline{H}CO_2Et$, $J=15$); 5,5–6,05 m (1H, $-C(\overline{CH_3})=C\underline{H}$); 7,45 d.d (1H, $-C\underline{H}=CHCO_2Et$, $J=11$, $J=15$) | 1710 (C=O)<br>1635 (C=C) | 279<br>(49000) |
| (II) | 64 | 130–134 (0,3) | 1,4775 | 0,87–1,42 m (14H, $2CH_3$, $4CH_2$); 1,54–1,90 m (9H, $(CH_3)_2C-$, $-C(CH_3)=$); 2,05–2,35 m (6H, $=C-CH_2CH_2-C=C-C=C-CH_2$); 4,10 q (2H, $CH_2-$ of ester $J=7$); 5,00 m (1H, $(CH_3)_2C=C\underline{H}$); 6,0 w.d (1H, $C(CH_3)=C\underline{H}$, $J=12$); 7,25 d (1H, $CH=C(C_6H_{13})$, $J=12$) | 1690 (C=O)<br>cis<br>1725 (C=O)<br>trans<br>1630 (C=C) | 283<br>(23000) |
| (III) | 60 | 120–122 (0,6) | 1,5520 | 1,25 t (3H, ester $CH_3$ $J=7$); 1,57–2,00 m (9H, $3CH_3$); 2,05–2,30 m (4H, $2CH_2$); 4,12 q (2H, $CH_2$ of ester $J=7$); 5,05 m (1H, $(CH_3)_2C=C\underline{H}$); 5,8 d (1H, $=C\underline{H}CO_2Et$, $J=15$); 5,85–6,80 m (3H, $C(CH_3)=C\underline{H}-C\underline{H}=C\underline{H}$); 7,3 d.d (1H, $C\underline{H}=CHCO_2Et$, $J=10$, $J=15$) | 1700 (C=O)<br>1612 (C=C) | 320<br>(57500) |
| (IV) | 57 | 120–121 (1,0) | 1,5050 | 1,11–1,95 m (16H, $4CH_3$, $2CH_2$); 2,20–2,65 m (1H, $(CH_3)_2\underset{\diagdown O \diagup}{C-C\underline{H}}$); 4,10 q (2H, $CH_2$ of ester $J=7$); 5,7 d (1H, $=C\underline{H}CO_2Et$, $J=15$); 5,8–6,1 (1H, $C(CH_3)=C\underline{H}$); 7,45 d.d (1H, $C\underline{H}=CHCO_2Et$, $J=11$, $J=15$) | 1710 (C=O)<br>1635 (C=C) | 218<br>(15900)<br>278<br>(29200) |
| (V) * | 59 | 148–150 (1,0) | 1,4700 | 0,88–1,72 m (29H, $5CH_3$, $7CH_2$); 2,20–2,50 m (1H, $(CH_3)_2\underset{\diagdown O \diagup}{C-C\underline{H}}-$); 3,15–3,40 m (1H, $(CH_3)\underset{\diagdown O \diagup}{C-C\underline{H}}$); 4,05 q (2H, $CH_2$ of ester $J=7$); 6,4 d, 6,36 d (1H, $C\underline{H}=C(C_6H_{13})$, $J=10$, $J=15$) | 1718 (C=O) | 230<br>(15300) |
| (VI) | 49 | 155–160 (1,0) | 1,4980 | 1,07–1,70 m (16H, $4CH_3$, $2CH_2$); 2,35–2,65 m (1H, $(CH_3)_2\underset{\diagdown O \diagup}{C-C\underline{H}}$); 3,15–3,30 m (1H, $(CH_3)\underset{\diagdown O \diagup}{C-C\underline{H}}$); 4,10 q (2H, ester $CH_2$ $J=7$); 5,85 d (1H, $=C\underline{H}CO_2Et$, $J=15$); 6,00–6,45 m (2H, $CH=CH$); 7,25 d.d (1H, $C\underline{H}=CHCO_2Et$, $J=10$, $J=15$) | 1710 (C=O) | 215<br>(12100)<br>267<br>(25600) |
| (VI)+(VII) | | | | 1,11–1,40 m ($CH_3$); 1,45–1,70 m ($CH_2$); 1,83 s ($C(CH_3)=$); 2,05–2,30 m ($=CH\underline{CH_2CH_2}C=$); 2,35–2,65 m ($(CH_3)_2\underset{\diagdown O \diagup}{C-C\underline{H}}$); 3,15–3,30 m ($(CH_3)\underset{\diagdown O \diagup}{C-C\underline{H}}$); 4,10 q ($CH_2$ of ester $J=7$); 5,80 d ($=C\underline{H}CO_2Et$, $J=15$); 5,85–6,80 m ($=CH-CH=CH$); 7,20 d.d ($C\underline{H}=CHCO_2Et$, $J=10$, $J=15$) | 1710 (C=O)<br>1742 (C=C) | 215<br>(10800)<br>267<br>(44000)<br>315<br>(23200) |

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*Found: C 71.33; H 10.24% $C_{20}H_{34}O_4$. Calculated: C 70.97; H 10.13%.

40-45.° The reaction mixture was let stand overnight, after which it was diluted with ether, washed with 5% NaOH solution, and dried over $MgSO_4$. After removal of the ether the residue was used as such in the next step.

c) To 150 ml of a mixture of AcOH, AcONa, and water was added the alkoxy acetal and the stirred mixture was heated at ∿100° for ∿3 h. After cooling, the mixture was diluted with water and extracted with ether. The ether extracts were washed with water and $NaHCO_3$ solution. After drying over $MgSO_4$ the product was isolated in 50% yield (based on the two steps) by fractional distillation, bp 85-95° (0.3 mm).

Esters of Acids (I), (II), and (III). To 0.1 mole of the phosphonate in 100 ml of abs. DMF was added a solution of $C_2H_5ONa$ in 50 ml of abs. alcohol (obtained from 2.3 g of Na), the mixture was stirred for 1 h, and then 0.1 mole of the aldehyde was added in drops in such manner that the temperature of the reaction mass did not exceed 36°. The next day the mixture was poured into water and extracted with ether. The ether extracts were dried over $MgSO_4$, and (I), (II), and (III) were isolated by fractional distillation (see Table 1).

Epoxidation of Esters (I), (II), and (III). To a mixture of 0.027 mole of phthalic anhydride, 0.009 mole of urea, and 0.009 mole of the ester in 15 ml of abs. ether was added in drops 0.027 mole of 87-90% $H_2O_2$. The reaction course was checked by TLC. The precipitate of phthalic acid was washed with ether, and the ether extracts were washed in succession with $NaHCO_3$ solution and water, and then dried over $MgSO_4$. Compounds (IV), (V), (VI), and (VII) were isolated by fractional distillation (see Table 1).

## CONCLUSIONS

The direction of the epoxidation of a number of polyunsaturated acids was studied and it was shown that the epoxidation proceeds at the double bonds furthest away from the carbethoxyl group.

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# RADICAL ARYLATION OF DISULFIDES

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A study of the action of radicals on disulfides is of great interest both as regards radical processes in the organosulfur series of compounds [1-3] and in biochemistry [1].

The reaction of phenyl and p-nitrophenyl radicals, generated by the decomposition of arylazotriphenylmethanes, with dialkyl disulfides was described in [1], while the action of benzyl radicals, obtained by the decomposition of tert-butyl peroxide in toluene, on diaryl disulfides was described in [2]. The purpose of these papers was to study the competing attack of the radicals on the sulfur atom on the hydrogen atoms in dialkyl disulfides according to the scheme:

$$RR'CHSSCHRR' + C_6H_5^{\cdot} - \begin{cases} \rightarrow RR'CHSC_6H_5 + RR'CHS^{\cdot} & (1a) \\ \rightarrow RR'\dot{C}SSCHRR' + C_6H_6 & (1b) \end{cases}$$

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