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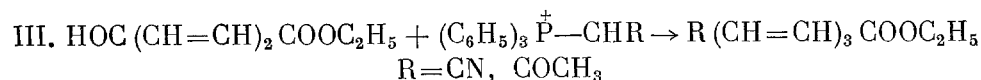
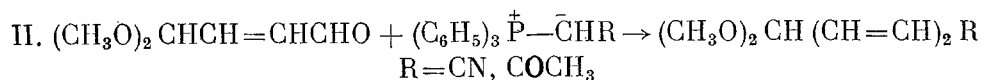
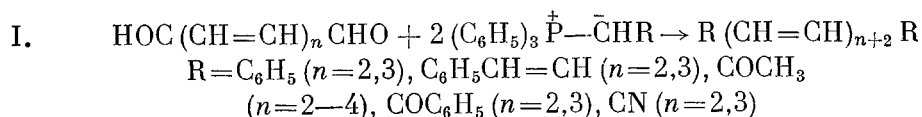
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We have previously developed simple ways of synthesizing polyenic dialdehydes of type $\text{HOC}(\text{CH}=\text{CH})_n\text{CHO}$ [1,2], fumaraldehyde monoacetal [3], and polyenic aldehydic esters of type $\text{HOC}(\text{CH}=\text{CH})_n\text{COOC}_2\text{H}_5$ [4]. This enabled us to suggest accessible methods for the preparation of various symmetrical and unsymmetrical polyenic dicarboxylic acids [4]. In the development of this work we were able to show that from the above-mentioned compounds by the aid of the Wittig reaction it is possible to prepare the most varied previously difficulty accessible symmetrical and unsymmetrical bifunctional polyenic compounds in accordance with the general schemes:



In this way we prepared the symmetrical diphenyl polyenes $\text{C}_6\text{H}_5(\text{CH}=\text{CH})_n\text{C}_6\text{H}_5$ ($n = 4-7$), the α,ω -diacetyl polyenes $\text{CH}_3\text{CO}(\text{CH}=\text{CH})_n\text{COCH}_3$ ($n = 4-6$), the α,ω -dibenzoyl polyenes $\text{C}_6\text{H}_5\text{CO}(\text{CH}=\text{CH})_n\text{COC}_6\text{H}_5$ ($n = 4-5$), the polyenic dinitriles $\text{NC}(\text{CH}=\text{CH})_n\text{CN}$ ($n = 4,5$), the dibromo polyenic esters $\text{C}_2\text{H}_5\text{OOCCH}=\text{CH}(\text{CH}=\text{CH})_n\text{CH}=\text{CHCBrCOOC}_2\text{H}_5$ ($n = 2,3$), and some unsymmetrical bifunctional polyenes: $(\text{CH}_3\text{O})_2\text{CH}(\text{CH}=\text{CH})_2\text{COCH}_3$, $(\text{CH}_3\text{O})_2\text{CH}(\text{CH}=\text{CH})_2\text{CN}$, $\text{C}_2\text{H}_5\text{OOC}(\text{CH}=\text{CH})_3\text{CN}$, and $\text{C}_2\text{H}_5\text{OOH}(\text{CH}=\text{CH})_3\text{COCH}_3$. The compounds obtained were characterized by their ultraviolet and infrared spectra. As would be expected, all the compounds obtained had all-trans configurations (absence of absorption bands in the region $700-850\text{ cm}^{-1}$).

EXPERIMENTAL

1,8-Diphenyl-1,3,5,7-octatriene (I). A solution of 0.059 g of lithium in 60 ml of absolute alcohol was added dropwise with stirring to a solution of 0.456 g of muconaldehyde and 3.5 g of benzyltriphenylphosphonium chloride in 30 ml of absolute alcohol. The mixture was stirred for 4 h, and on the next day the crystals that had precipitated were separated. Crystallization from benzene gave 0.24 g (24%) of (I), m.p. $228-230^\circ$, λ_{max} (in benzene) 362, 380, 403. Literature data [5] gives m.p. 232° (corrected).

1,10-Diphenyl-1,3,5,7,9-decapentaene was prepared like (I) from 0.8 g of 2,4,6-octatrienedial; yield 0.57 g (34.7%); m.p. $249-250^\circ$, λ_{max} (in benzene) 381, 401, 425. Literature data [5] gives m.p. 253° .

1,12-Diphenyl-1,3,5,7,9,11-dodecahexaene was prepared like (I) from 0.81 g of muconaldehyde and cinnamyltriphenylphosphonium bromide; yield 0.31 g (31%); m.p. $260-262^\circ$ (decomp.); λ_{max} 398, 418, 446. Literature data [5] gives m.p. 267° (decomp.).

1,14-Diphenyl-1,3,5,7,9,11,13-tetradecaheptaene was prepared like (I) from 1.12 g of 2,4,6-octatrienedial and cinnamyltriphenylphosphonium bromide (the phosphorane was liberated with alcoholic sodium ethoxide solution); the yield was 0.39 g (13%); m.p. 275-276° (decomp.; from chloroform), λ_{\max} (in benzene) 412, 436, 464. Literature data [5] gives m.p. 279° (decomp).

3,5,7,9-Dodecatetraene-2,11-dione (II). A solution of 0.588 g of muconaldehyde and 3.5 g of acetonilydene-triphenylphosphorane in 25 ml of benzene was heated for 6 h at 60-70°. Benzene was driven off, the residue was treated with 15 ml of alcohol, and the crystals were filtered off and recrystallized from alcohol. We obtained 0.16 g (17%) of (II), m.p. 143-144°, λ_{\max} (in alcohol) 257.5 (ϵ 3800), 351 (ϵ 62,600). Found: C 75.52, 75.67; H 7.39, 7.45%. $C_{12}H_{14}O_2$. Calculated: C 75.76; H 7.42%.

3,5,7,9,11-Tetradecapentaene-2,13-dione was prepared from 0.68 g of 2,4,6-octatrienedial and 7 g of acetonilydenetriphenylphosphorane in 45 ml of toluene (boiling for 5.5 h); yield 0.65 g (60%); m.p. 166-168° (purified by filtering a solution of the diketone in methylene chloride through a 15-cm column of alumina and crystallization from alcohol); λ_{\max} (in alcohol) 284 (ϵ 6210), 380.5 (ϵ 25,100), 398 (ϵ 24,650). Found: C 77.61, 77.40; H 7.68, 7.72%. $C_{14}H_{16}O_2$. Calculated: C 77.79; H 7.46%.

3,5,7,9,11,13-Hexadecahexaene-2,15-dione was prepared like (II) from 0.31 g of 2,4,6,8-decatetraenedial and 1.273 g of acetonilydenetriphenylphosphorane in 25 ml of benzene (boiling for 6 h). It was purified by filtering its solution in methylene chloride through a 12-cm column of alumina and crystallization from alcohol; yield 0.26 g (57%); m.p. 196-197°, λ_{\max} 392 (ϵ 39,200), 406 (ϵ 52,500), 428 (ϵ 51,400). Found: C 79.11, 78.98; H 7.93, 7.93%. $C_{16}H_{18}O_2$. Calculated: C 79.31; H 7.49%.

1,10-Diphenyl-2,4,6,8-decatetraene-1,10-dione (III). A solution of 0.399 g of muconaldehyde and 2.66 g of phenacylidenetriphenylphosphorane in 30 ml of benzene was heated for 12 h at 60-70°. The mixture was cooled, and the crystals that had precipitated were filtered off. We obtained 0.702 g (66%) of (III), m.p. 185-186° (from alcohol) and λ_{\max} (in alcohol) 385. Found: C 84.26, 84.06; H 6.05, 5.83%. $C_{22}H_{18}O_2$. Calculated: C 84.03; H 5.77%.

1,12-Diphenyl-2,4,6,8,10-dodecapentaene-1,12-dione was prepared like (III) from 0.408 g of 2,4,6-octatrienedial and phenacylidenetriphenylphosphorane in benzene (boiling for 7.5 h) and was recrystallized from glacial acetic acid; yield 0.62 g (62%); λ_{\max} (in alcohol) 415. Found: C 84.33, 84.13; H 6.12, 5.99%. $C_{24}H_{20}O_2$. Calculated: C 84.68; H 5.92%.

2,4,6,8-Decatetraenedinitrile (IV). A solution of 0.456 g of muconaldehyde and 3.01 g of (triphenylphosphoranylidene)acetonitrile in 25 ml of benzene was heated for 14 h at 65-70°. The resulting crystals were filtered off and washed with alcohol; they were recrystallized from a mixture of benzene and pentane. We obtained 0.21 g (37%) of (IV), m.p. 196-198°, λ_{\max} (in alcohol) 314 (ϵ 59,800), 330 (ϵ 89,200), 346 (ϵ 88,600). Found: C 76.90, 76.70; H 4.97, 5.07; N 17.76%. $C_{10}H_8N_2$. Calculated: C 76.90; H 5.16; N 17.94%.

2,4,6,8,10-Dodecapentaenedinitrile was prepared like (IV) from 0.57 g of 2,4,6-octatrienedial and (triphenylphosphoranylidene)acetonitrile in benzene (heating at 60° for 4 h and boiling for 3 h). For purification a solution of the product in methylene chloride was filtered through a 15-cm column of alumina. We obtained 0.4 g (52%) of product, m.p. 213-214°, λ_{\max} (in alcohol) 265 (ϵ 4160), 342 (ϵ 54,500), 359 (ϵ 92,100), 379 (ϵ 94,100). Found: C 78.81, 78.72; H 5.56, 5.36%. $C_{12}H_{10}N_2$. Calculated: C 79.09; H 5.53%.

Diethyl 2,9-Dibromo-2,4,6,8-decatetraenedioate (V). A solution of 0.227 g of muconaldehyde and 1.88 g of ethyl bromo(triphenylphosphoranylidene)acetate in 30 ml of benzene was heated at 60-70° for 10 h. Benzene was driven off, and the residue was treated with 5 ml of acetone and filtered off. We obtained 0.48 g (63%) of (V), m.p. 175-176° (from alcohol), λ_{\max} (in alcohol) 362 (ϵ 48,500), 379 (ϵ 42,000). Found: C 41.71, 41.82; H 3.94, 4.02; Br 38.74, 38.66%. $C_{14}H_{16}O_4Br_2$. Calculated: C 41.18; H 3.95; Br 39.17%.

Diethyl 2,11-Dibromo-2,4,6,8,10-dodecapentaenedioate was prepared like (V) from 0.325 g of 2,4,6-octatrienedial and ethyl bromo(triphenylphosphoranylidene)acetate in benzene (boiling for 6 h); it was recrystallized from alcohol. Yield 0.8677 g (50%); m.p. 161-162°, λ_{\max} (in alcohol) 386 (ϵ 80,000), 408 (ϵ 69,000). Found: C 44.01, 44.14; H 4.11, 4.19; Br 34.62, 34.78%. $C_{16}H_{18}O_4Br_2$. Calculated: C 44.26; H 4.17; Br 34.28%.

5-Cyano-2,4-pentadienal Dimethyl Acetal (VI). A solution of 6.5 g of fumaraldehyde mono[dimethyl acetal] and 15 g of (triphenylphosphoranylidene)acetonitrile in 100 ml of dimethylformamide was heated for 20 h at 60°. The solution was vacuum-evaporated, the residue was extracted with ether, and the extract was filtered through a layer of alumina. Fractionation gave 1.3 g (20%) of (VI), b.p. 83-86° (3 mm); n_D^{20} 1.4970. Found: C 62.71, 62.85; H 7.13, 7.29%. $C_8H_{11}O_2N$. Calculated: C 62.72; H 7.24%.

On treatment with a solution of 2,4-dinitrophenylhydrazine in 2 N HCl, the product gave a red 2,4-dinitrophenylhydrazone, m.p. 201-203° (from a mixture of alcohol and ethyl acetate). Found: N 23.97, 24.05%. $C_{12}H_9O_4N_5$. Calculated: N 24.38%.

6-Oxo-2,4-heptadienal Dimethyl Acetal was prepared like (VI) from 6.5 g of fumaraldehyde mono[dimethyl acetal] and 15.5 g of acetonylidenetriphenylphosphorane. Yield 3 g (35%), b.p. 94° (3 mm), n_D^{20} 1.5040. Found: C 63.86, 63.90; H 8.40, 8.36%. $C_9H_{14}O_3$. Calculated: C 63.51; H 8.29%.

On treatment with a solution of 2,4-dinitrophenylhydrazine in 2 N HCl it gave a red 2,4-dinitrophenylhydrazone, m.p. 203-206° (from a mixture of alcohol and ethyl acetate), which according to carbon and hydrogen determinations was the mono(2,4-dinitrophenylhydrazone) obtained by reaction at the aldehyde grouping. Found: C 51.25, 51.50; H 4.09, 4.13%. $C_{13}H_{12}O_5N_4$. Calculated: C 51.31; H 3.98%.

Ethyl 7-Cyano-2,4,6-heptatrienoate (VII). A solution of 4 g of ethyl 5-formyl-2,4-pentadienoate and 6 g of (triphenylphosphoranylidene)acetonitrile in 100 ml of benzene was heated for 24 h at 60°. Benzene was vacuum-distilled off, the residue was extracted with ether, the extract was filtered twice through a layer of alumina, ether was removed, and the residue was recrystallized from a mixture of petroleum ether and benzene. We obtained 3.5 g of crystals, m.p. 78.5-81.5°, λ_{max} (in alcohol) 222 (ϵ 10,100), 299 (ϵ 28,100), 311 (ϵ 24,400). Found: C 68.17, 68.03; H 6.71, 6.50%. $C_{10}H_{11}O_2N$. Calculated: C 67.78; H 6.26%.

Ethyl 8-Oxo-2,4,6-nonatrienoate was prepared like (VII) from 4 g of ethyl 5-formyl-2,4-pentadienoate and 7 g of acetonylidenetriphenylphosphorane. Yield 4 g; m.p. 67-69° (from aqueous alcohol, and then from petroleum ether), λ_{max} (in alcohol) 310 (ϵ 43,000). Found: C 65.84, 65.77; H 7.70, 7.51%. $C_{11}H_{14}O_3$. Calculated: C 65.91; H 7.74%. The substance was very unstable to keeping at room temperature.

Treatment with a solution of 2,4-dinitrophenylhydrazine in 2 N HCl gave a red 2,4-dinitrophenylhydrazone, m.p. 170-172° (from alcohol). Found: N 15.30, 15.39%. $C_{17}H_{18}O_6N_4$. Calculated: N 14.97%.

SUMMARY

Some symmetrical and unsymmetrical bifunctional polyenic compounds were synthesized; they included diphenyl polyenes, polyenic diketones and dinitriles, dibromo polyenic dicarboxylic esters, polyenic cyano acetals and keto acetals, polyenic keto esters, and cyano polyenic carboxylic esters.

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