the uv absorption and Cotton effect are in the region 230–240 mμ[14,15,18] and no absorption at longer wavelengths corresponding to n → π^* transitions of the >C=N– group have been reported.

As well as the low intensity long wavelength bands which we have attributed to n → π^* transitions of the carbonyl groups, our uv spectra also show for **3** a maximum at 235 mμ and for **2** a shoulder at approximately 220 mμ.

While it proved impossible to obtain the relative proportions of the two isomers formed from the chromatographic separation due to partial overlap of dimethylfuroxan, we have obtained the relative proportions from the nmr spectrum of the crude reaction product. Since both **2** and **3** contribute to the signal at δ 5.4 (in the ratio of 1:2) while only **2** contributes to the signal at δ 3.84, from the relative intensities of these two signals we calculated the product ratio of **2**:**3** as 9:1.

Registry No.—**1**, 979-02-2; **2**, 1057-99-4; **3**, 1253-19-6.

Preparation of 1,6-Diarylhexatrienes by a Modified Wittig Reaction

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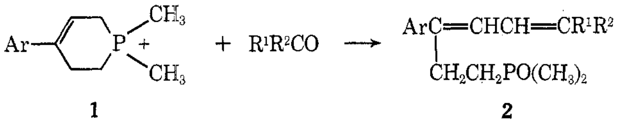
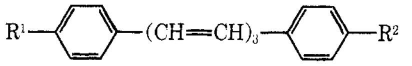
Recently we showed that reaction of cyclic phosphonium salts such as **1** with strong base followed by treatment of the resulting ylide with carbonyl compounds afforded a series of phosphorus-containing dienes.[1]



1 **2**

Prompted by the availability of a good method for the preparation of 1-methyl-3-phospholene,[2] we decided to investigate the behavior of the corresponding methiodide under the conditions of the Wittig reaction. Initial attempts to translate directly the reaction conditions used in the earlier work were not promising. When, however, a mixture of the salt and benzaldehyde was treated with 2 equiv of *tert*-butoxide in THF there was obtained on work-up an extremely insoluble crystalline compound. The absence of any PCH_3 bands in the nmr suggested that this was not a product analogous to **2**. The mass and uv spectra of the crude product both indicated this to be a mixture of isomeric 1,6-diphenylhexatrienes. Recrystallization afforded a pure sample of the polyolefin whose properties are in agreement with those recorded in the literature.[3] By carefully adjusting conditions it proved possible to obtain this product in 26% yield by direct crystallization. Table I records results of this condensation employing several aldehydes.

TABLE I

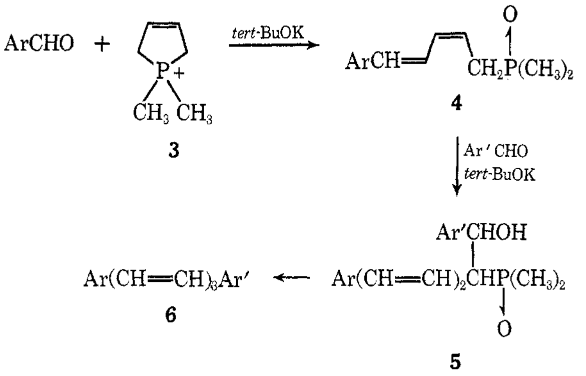


R^1	R^2	Registry no.	Mp, °C	Lit mp, °C	Yield, %
H	H	1720-32-7	194–197	199–201[a]	26
CH_3	CH_3	31382-31-7	229–231		10[b]
OCH_3	OCH_3	31382-32-8	250–250.5	247–248[c]	17

[a] See ref 3. [b] *Anal.* Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.69; H, 7.70. [c] K. Friedrich and W. Hartmann, *Chem. Ber.*, **94**, 840 (1961).

The overall transformation can be rationalized by some scheme such as that shown in Scheme I. The first step is simply analogous to the overall reaction demonstrated in the earlier work. The product **4** in this case, however, contains an active methylene group which should undergo an aldol condensation with a second mole of aldehyde to form the corresponding triene.[4]

SCHEME I



In order to test the validity of Scheme I, the quaternary salt **3** was treated with a single equivalent of base and tolualdehyde. The product was carefully worked up and chromatographed to afford a small amount of triene and a very polar gummy fraction. The mass spectrum (*m/e* 234.1175) and nmr (Ar H, 4 H at δ 7.2; vinyl protons 4 H δ 6–7; $ArCH_3$, 3 H at δ 2.3; PCH_3, 6 H, multiplets at δ 1.3 and 1.5) of the gum are in accord with a mixture of isomers of the intermediate **4**. Exposure of the gum to 1 equiv of potassium *tert*-butoxide and benzaldehyde gave the mixed triene, albeit in low yield (**6**, Ar = C_6H_5; Ar′ = p-$CH_3C_6H_4$), as the sole identifiable product. This then in broad outline provides evidence for the above scheme.

Experimental Section[5]

1-Methyl-3-phospholene Methiodide (3).—Methyldichlorophosphine (50 g) was added to a solution of 23 g of butadiene in

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[1] D. Lednicer, *J. Org. Chem.*, **35**, 2307 (1970).

[2] L. D. Quin and J. A. Peters, *Tetrahedron Lett.*, 3689 (1964).

[3] R. Kuhn and A. Winterstein, *Helv. Chim. Acta*, **11**, 87 (1928).

[4] See, for example, T. H. Kinstle and B. Mendanas, *Chem. Commun.*, 1699 (1968).

[5] Melting points are uncorrected and recorded as obtained on a Thomas-Hoover capillary melting point apparatus. Nmr spectra were determined in deuteriochloroform on a Varian A-60 spectrometer. The author is indebted to the Department of Physical and Analytical Chemistry of The Upjohn Co. for elemental and spectral determinations.

200 ml of hexane under N_2 in a drybox. At the end of 10 days, operating again in a drybox under nitrogen, the solid (33 g) was collected on a filter and transferred to a 1-l. three-necked flask. THF (400 ml) and Mg (6.5 g) were then added and the mixture (under N_2) was heated at reflux. 1,2-Dibromoethane (1 ml) was added and heating was continued for 16 hr. The mixture was allowed to cool and treated in turn with 40 ml of concentrated HCl and 30 ml of H_2O. The THF was then removed in vacuum, and the residue was made strongly basic and steam distilled. The distillate (250 ml) was extracted with ether.

The ether extract was dried over Na_2SO_4 and then treated with 10 ml of methyl iodide. At the end of 4 hr the precipitate was collected on a filter. One crystallization from acetonitrile-ether gave 10.15 g of solid, mp 287–290°.

Anal. Calcd for $C_6H_{12}IP$: C, 29.77; H, 5.00. Found: C, 29.87; H, 4.95.

Condensation Reaction.—In a typical run 2.36 g (0.01 mol) of the finely powdered methiodide **3** was added over 5 min to a mixture of 0.02 mol of the appropriate aldehyde and 2.24 g (0.02 mol) of *tert*-BuOK in 100 ml of THF. The mixture was stirred at room temperature for 5 hr and the solvent was then removed *in vacuo*. The residue was treated with H_2O and the precipitated gum recrystallized from an appropriate solvent.

1-Phenyl-6-(*p*-tolyl)-1,3,5-hexatriene (6).—To a well-stirred suspension of 4.72 g (0.02 mol) of the methiodide **3** and 2.40 g (0.02 mol) of tolualdehyde in 200 ml of THF there was added in portions 2.24 g (0.02 mol) of *tert*-BuOK. Following 1 hr of stirring at room temperature and 4 hr at reflux the solvent was removed *in vacuo*. The residue was treated with H_2O and Et_2O. There was obtained 0.20 g of crude symmetrical bistolyl triene, mp 220–230°. The gum obtained from the Et_2O layer was chromatographed on 300 ml of Florisil[6] (elution with 20% Me_2CO in Skellysolve B[7] followed by 100% Me_2CO); the last solvent brought over 0.80 g of **4** (Ar = p-$CH_3C_6H_4$) as a viscous gum.

A mixture of the above gum was allowed to react as above with 0.50 ml of benzaldehyde and 0.40 g of *tert*-BuOK in 25 ml of THF. The oily solid obtained on work-up was chromatographed on 100 ml of silica gel (elution with 5% Me_2CO in Skellysolve B). The solid fractions were combined and recrystallized from Skellysolve B to afford 70 mg of triene, mp 192.5–195°.[8]

Anal. Calcd for $C_{19}H_{18}$: C, 92.63; H, 7.37; mass spectrum (m/e) 246.1408. Found: C, 92.51; H, 7.34; mass spectrum (m/e) 246.1396.

Registry No.—**3**, 18005-44-2; **6**, 31382-34-0.

[6] A synthetic magnesia silica gel absorbent from the Floridin Co., Warren, Pa.

[7] A petroleum fraction, bp 60–70°, sold by the Skelly Oil Co.

[8] Lit. mp 195–196°: B. M. Mikhailov and L. S. Pardrov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 839 (1959).