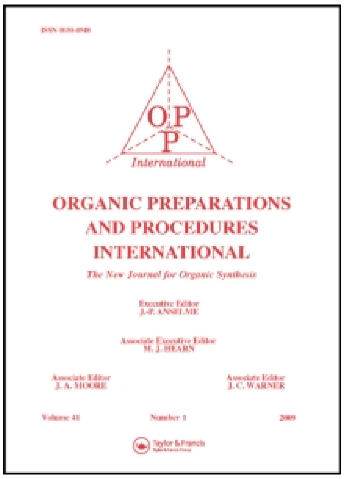

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HEXAARYLVINYLFULVENES

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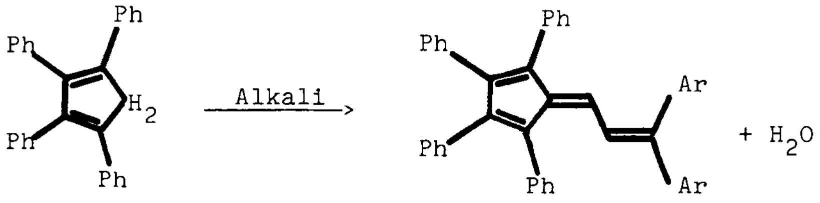
$$\underset{\text{III a-d}}{Ar_2C{=}CH_2} + HCON(CH_3)Ph \xrightarrow{POCl_3} \underset{\text{II a-d}}{Ar_2C{=}CH{-}CHO} + PhNH(CH_3) \qquad (1)$$



(2)

a. Ar = C_6H_5
b. = p-ClC_6H_4-
c. = p-$CH_3OC_6H_4$-
d. = p-$(CH_3)_2NC_6H_4$-

No vinyl analogs of hexaphenylfulvene (I) have been reported. Yet the parent hydrocarbon is colored and, predictably, the substituted vinylfulvenes would also be colored. In this paper we report the synthesis of four vinylfulvenes, their electronic spectra, and comment on the synthesis of their precursor 1,1-diarylethylenes.

The synthetic route chosen was the formylation of the 1,1-diarylethylenes (III) to give the 3,3-diarylacroleins (II) via the Vilsmeier reaction (Eq. 1) followed by base-catalyzed condensation with tetraphenylcyclopentadiene to give the 6-(2',2'-diarylvinyl)-1,2,3,4-tetraphenylfulvenes (I) (Eq. 2).

The 1,1-diarylethylenes were prepared by either of two methods. IIIa and IIIc were prepared by dehydration of the carbinols resulting from the addition of the appropriate Grignard reagents to ethyl acetate.[3,4] In neither case was it necessary to isolate the carbinol before dehydration. Attempts to prepare IIId by this method were unsuccessful since the required p-dimethylaminophenylmagnesium bromide or iodide could not be prepared by the usual techniques for Grignard reagents. The Ehrlich and Sachs method[5] was also unsuccessful.

IIIb and IIId were prepared by dehydration of the carbinols resulting from the addition of methylmagnesium iodide[4] to the corresponding benzophenones. Isolation of the carbinol prior to dehydration was optional.

Compounds II were prepared by the methods described by Lorenz and Wizinger[7] or Carpmael[8] in which the corresponding diarylethylenes were treated with N-methylformanilide in the presence of phosphorus oxychloride (see Table I). 3,3-Diphenylacrolein and 3,3-bis-(p-dimethylaminophenyl)acrolein were prepared without difficulty with good yields. The preliminary purification of the 3,3-bis(p-chlorophenyl)acrolein required distillation below 5 mm. to avoid resinification.

Table I

Preparation of 3,3-Bis(p-Substitutedaryl)acroleins

Acrolein	Reactants Moles			M.P.,	Yield,	2,4-Dinitro-Phenyl-Hydrazone
	Diaryl-ethylene	$POCl_3$	C_8H_9NO	°C.	%	M.P., °C.
IIa	0.088	0.200	0.148	42-43[a,b]	53.1	196-196.5[c]
b	0.084	0.200	0.148	205-206	35.0	203-203.5
c	0.033	0.105	0.033	------[d]	40.0	205-207[e]
d	0.038	0.229	0.200	171-172[f]	42.0	255-256[g]

[a] Reported (7): 44°.

[b] B.p. 205-207° (15 mm) reported (5): 205-210° (14 mm)

[c] Reported (5): 195-196°.

[d] A viscous oil which decomposed on distillation. The crude contained 90% of the acrolein which was identified as its 2,4-dinitrophenylhydrazone. Calcd. for $C_{23}H_{20}N_4O_6$: C, 61.60; H, 4.50; N, 12.49. Found: C, 61.40; H, 4.75; N, 12.50.

[e] Reported (5): 206-207°.

[f] Reported (5): 171-172°.

[g] Reported (5): 256-257°.

The 3,3-bis(p-anisyl)acrolein was not isolated in a pure state since distillation of the crude oil even at very low pressure led to resinification without appreciable recovery of the acrolein. Attempts to isolate the acrolein by crystallization from benzene, petroleum ether, carbon tetrachloride, alcohol, dioxane, and other solvents did not yield a solid product. A viscous oil was obtained upon decomposition of the bisulfite addition product. Repeated handling of the crude product also led to resinification. The identity and purity of a freshly prepared crude product was established by conversion to the 2,4-dinitrophenylhydrazone. The average crude contained 85-90% of 3,3-bis(p-anisyl)acrolein and was used in further steps in this form with satisfactory results.

Compounds I were prepared essentially by the procedure of Dilthey and Huchtemann[9] in which 2,3,4,5-tetraphenylcyclopentadiene was condensed with a carbonyl compound in the presence of an alkali, such as sodium methoxide in methanol. The condensations using the 3,3-diarylacroleins in methanolic sodium hydroxide proceeded without difficulty (see Table II and III). The yield of Ia was substantially improved from 50.0% to 86.3% by increasing the catalyst concentration from 2% to 4-6%. Compounds I were readily soluble in aliphatic

Table II

Vinylogues of Hexaphenylfulvene

Compounds I	Reactants (moles x 10^3)		M.P. °C.	Yield, %	Fluorescence[b]
	Acrolein (II)	TCP[a]			
a	10.80	2.70	252-253	88	Red
b	11.33	2.48	261-262	70	Red
c	8.39	2.70	235-237	54	Red
d	8.52	3.24	142-143	66	Red

[a] Tetraphenylcyclopentadiene

[b] In benzene or on alumina

Table III

Analyses, %

Compounds I	Calcd.				Found			
	C	H	Cl	N	C	H	Cl	N
a	94.25	5.75	-	-	94.20	5.81	-	-
b	83.94	4.80	11.26	-	84.16	4.80	11.16	-
c	89.00	5.85	-	-	89.14	5.83	-	-
d	89.13	6.54	-	4.33	89.36	6.19	-	4.45

hydrocarbons, but were insoluble in alcohol and other polar solvents. The dimethylamino derivative, Id, was sufficiently polar to be soluble in both aromatic hydrocarbons and in alcohol. Compounds I were fluorescent in benzene and when adsorbed on alumina (see Table IV).

Table IV

Spectral Characteristics of Vinylogues of Hexaphenylfulvene[a,b,c]

Compound	λ_1	ε_1	λ_2	ε_2	λ_3	ε_3
Ia	260	4.05	390	3.60	510	0.28
Ib	264	2.92	402	3.40	545	0.30
Ic	264	2.50	420	3.85	-	-
Id	243	3.15	343	1.72	450	1.65

[a] Cyclohexane at a concentration of 0.5 x 10^{-4} moles/l.

[b] λ_{max} are in mμ

[c] ε_{max} are x 10^4

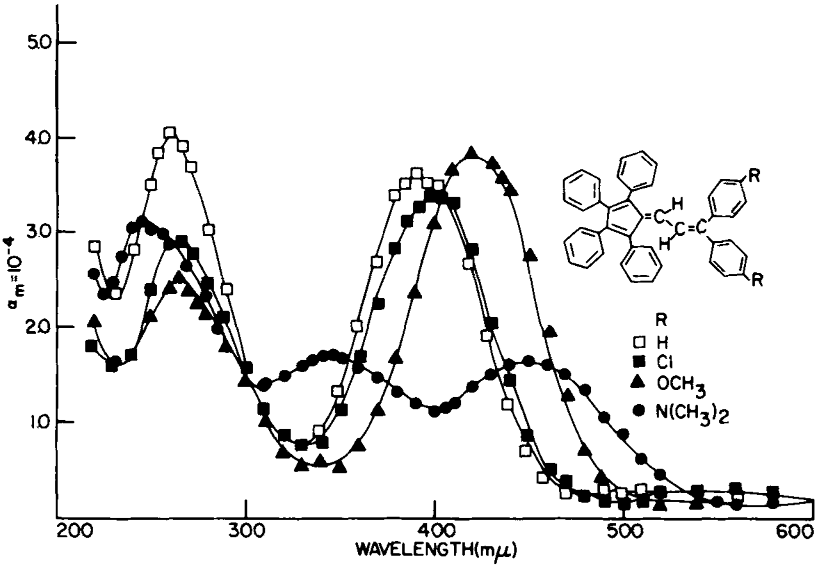


FIG. 1
Absorption Spectra of Some 6-Substituted Fulvenes

The absorption spectra were determined in a Beckman Model DU ultraviolet-visible spectrophotometer using 1-cm. quartz cells and a concentration of 0.5 x 10^{-4} molar in cyclohexane (see Fig. 1 and Table IV).

EXPERIMENTAL

All melting points are corrected.

Starting Materials. - 1,1-Diphenylethylene, b.p. 124-125° (5 mm), d_4^{20}1.036, n_D^{20}1.613, was prepared by the dry distillation of the carbinol derived from the reaction of phenylmagnesium bromide with ethyl acetate.[3] 1,1-Bis(*p*-chlorophenyl)ethylene (m.p., 84.5-85.5°) was prepared by the dehydration of the carbinol derived from the reaction of methylmagnesium iodide and 4,4'-dichlorobenzophenone.[6] 1,1-Bis(*p*-anisyl)-

ethylene (m.p., 142-143°) was prepared from the reaction of p-anisylmagnesium bromide and ethyl acetate with or without the isolation of the intermediate carbinol.[4] 1,1-Bis(p-dimethylaminophenyl)ethylene (m.p., 120-122°) was prepared from methylmagnesium iodide and tetramethyldiaminobenzophenone with separation of the intermediate carbinol.[4] 2,3,4,5-Tetraphenylcoclopenta-2,4-diene (m.p., 179-180°) was prepared according to Ziegler and Schnell.[10]

Diarylacroleins. - The 3,3-diarylacroleins were prepared by the methods described by Lorenz and Wizinger[7] and Carpmael[8] in which the corresponding diarylethylenes were treated with N-methylformanilide in the presence of phosphorus oxychloride. The quantities of reagents used are recorded in Table I. A typical procedure is given here since in the literature the purification is described separately from preparation of the crude.

3,3-Diphenylacrolein. - N-Methylformanilide (20 g., 0.148 moles) was added dropwise to phosphorus oxychloride (30 g., 0.20 moles) over a period of 2 hr. at room temperature. 1,1-Diphenylethylene (16 g., 0.089 moles) was then added dropwise and the mixture stirred for 24-48 hr. at room temperature. The excess phosphorus oxychloride was then destroyed by pouring the reaction mixture onto ice, the mixture made alkaline with sodium hydroxide and distilled with steam to remove N-methylaniline. After taking up the oily residue in benzene, the solution was dried with calcium chloride, and distilled under reduced pressure to give a pale yellow oil, b.p. 205-207° (15 mm.). An ether solution of the oil was shaken with a saturated solution of sodium bisulfite, and the addition product filtered and washed with ether. Shaking the solid with 3% sodium carbonate solution followed by crystallization from petroleum ether (b.p. 40-50°) gave pale yellow crystals of the product, 9.78 g. (0.047 moles, 53%).

The 2,4-dinitrophenylhydrazone was prepared in the usual manner, m.p. 196.0-196.5° [reported: 195-196°;[7] 203-204°;[11] 207°[12]].

Vinyl Analogs of Hexaphenylfulvene. - The procedure employed was adapted from that of Dilthey, et al.,[9] in which 2,3,4,5-tetraphenylcyclopentadiene was condensed with a para-substituted benzaldehyde in the presence of sodium methoxide. The quantities of reagents used are reported in Table II. A typical procedure is given here.

2,3,4,5-Tetraphenyl-6-(2',2'-diphenylvinyl)fulvene. - To a solution of 3,3-diphenylacrolein (2.25 g., 10.8 mmole in 25 ml. of anhydrous methanol was added 2,3,4,5-tetraphenylcyclopentadiene (1.0 g., 2.7 mmoles) and 25 ml. of an 80% solution of sodium methoxide in anhydrous methyl alcohol. The mixture was refluxed for 3 hr. after which time a reddish brown granular precipitate separated. The product was dissolved in benzene and chromatographed on alumina (Aluminum Company of American, grade F-20) and eluted with a 5% solution of methyl alcohol in benzene. The product fluoresced red under ultraviolet light.

After distillation of the solvent from the eluate, the product was crystallized twice from petroleum ether (b.p. 40-50°) to give reddish brown crystals, 1.33 g., m.p. 252-253°), (2.33 mmole; 88%).

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