

Preparation and Properties of 1,1-Diaryl-1,3-butadienes

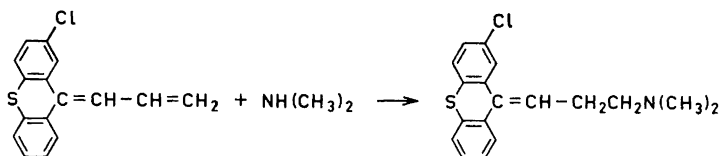
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The amine elimination from the methiodides of N,N-dimethyl-4,4-diaryl-3-butenylamines is shown to be an efficient route to the highly reactive 1,1-diaryl-1,3-butadienes. The intermediate amines are obtained by Grignard reaction of γ -dimethylaminopropylmagnesium chloride with a benzophenone and subsequent dehydration of the benzhydrols obtained. 18 Diarylbutadienes were prepared by application of the method; the physical properties of the new compounds including the ultraviolet absorption spectra are discussed.

The preparation of 1,1-diaryl-1,3-butadienes has been accomplished by various methods. Lipp *et al.*¹ in an attempt to prepare diphenylmethylenecyclopropane obtained a product with the properties of diphenylbutadiene. They failed to prepare diphenylbutadiene by dehydration of diphenylallylcarbinol. Normant and Maitte² described the addition of propenylmagnesium chloride to benzophenone yielding the propenylbenzhydrol which by losing water and rearranging spontaneously gave 1,1-diphenyl-1,3-butadiene (I) as an oil, partly polymerizing during distillation. Duffner³ reported the Wittig reaction of triphenylmethylenephosphine with β,β -diphenylacrolein to give (I).

Kefalas⁴ in a patent described the preparation of 9-allylideneoxanthenes and 9-allylideneethioxanthenes by elimination of water from substituted 9-allyloxanthanol-9 and 9-allylthioxanthanol-9. The oily butadienes were not purified. The patent also described the amination of 9-allylidene-2-chlorothioxanthene with dimethylamine and certain other secondary amines, which led to 9- γ -dialkylaminopropylidene-2-chlorothioxanthene:



A further study of this reaction seemed of interest, and since the already known methods for preparation of diarylbutadienes were not satisfactory, it has been the purpose of this investigation to prepare and to characterize the pure

compounds. The preparation of 18 diarylbutadienes and their properties including ultraviolet data is now reported. They comprise eight *p,p'*-substituted 1,1-diphenyl-1,3-butadienes and ten diarylbutadienes in which the benzene rings are fused to threecyclic ring systems as in fluorene, xanthene, thioxanthene, 9,9-dimethyldihydroanthracene, dibenzocycloheptadiene, and dibenzocycloheptatriene. The formulas are shown in Fig. 1:

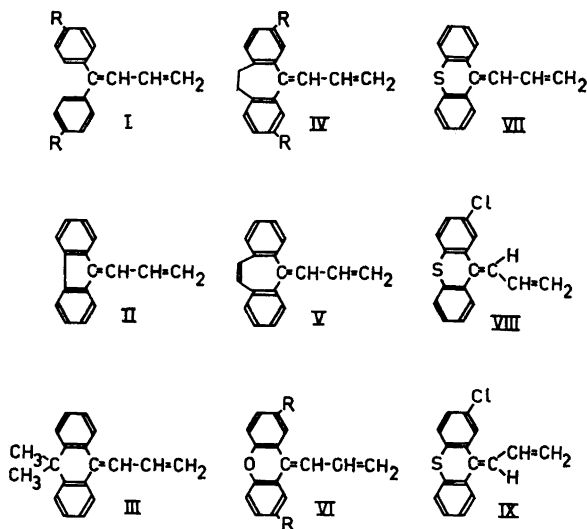


Fig. 1.

The chemical reactivity of these highly conjugated compounds and its dependence on substitution will be described in a subsequent paper.

A general and very convenient route to the diarylbutadienes was found in the Hofmann elimination of trimethylamine from the methiodides of 4-dimethylamino-1,1-diarylbutenes. These salts were obtained in a three-step

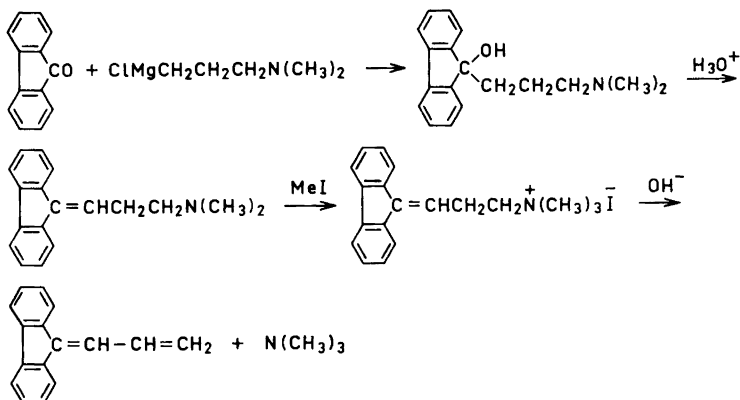


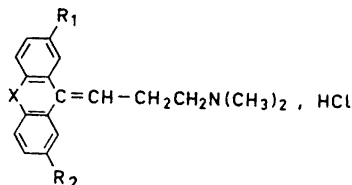
Fig. 2.

Table 1a. Hydrochlorides of N,N-dimethyl-4,4-diphenyl-3-butenylamines. Melting points of 4-dimethylamino-1,1-diphenyl-1-butanols (hydrol)

R*	M.p. °C	Formula	C		H		Cl		Hydrol. M.p. °C
			Found	Calc.	Found	Calc.	Found	Calc.	
H	179–180	C ₁₈ H ₂₂ ClN	74.95	75.08	7.74	7.72	12.66	12.34	118–120
F	170–172	C ₁₈ H ₂₀ F ₂ ClN	66.45	66.73	6.23	6.24	10.82	10.97	111–113
Cl	188–189	C ₁₈ H ₂₀ Cl ₂ N	60.25	60.56	5.66	5.66	29.98	29.86	102–103
Br	206–207	C ₁₈ H ₂₀ Br ₂ ClN	48.20	48.46	4.70	4.53	7.97	7.96	120–126
CH ₃	238–240	C ₂₀ H ₂₆ ClN	75.80	76.00	8.43	8.32	11.33	11.24	92–93
(CH ₃) ₃ C	261–263	C ₂₆ H ₃₈ ClN	77.70	78.00	9.50	9.60	9.10	8.89	120–121
CH ₃ O	175–177	C ₂₀ H ₂₆ ClNO ₂	68.27	69.01	7.62	7.56	10.35	10.21	89–90
(CH ₃) ₂ N	226–228	C ₂₂ H ₃₀ N ₂	70.45	70.63	8.71	8.64	9.34	9.50	141–142

* R = substituent at *p,p'* positions.

Table 1b. Hydrochlorides of threecyclic N,N-dimethyl-4,4-diaryl-3-butenylamines of the general formula:



X	R ₁	R ₂	m.p. °C	m.p. rep. °C
<i>o,o'</i> -bond	H	H	205–206	206–207 ⁶
CH ₃ C-CH ₃	H	H	242–245	245–248 ¹⁴
-CH ₂ CH ₂ -	H	H	195–196	197–199 ¹⁵
-CH ₂ CH ₂ -	Br	Br	246–248*	
-CH=CH-	H	H	213–215	216–217 ¹⁵
-O-	H	H	200–202	201–203 ⁶
-O-	Br	Br	222–223**	
-S-	H	H	180–182	181–183 ⁶
-S-	Cl	H	216–218	207–208 ¹⁶
-S-	H	Cl	224–225	223–224 ¹⁶

* Found: C 51.00; H 4.47; N 3.19. Calc. for C₂₀H₂₂Br₂ClN: C 50.88; H 4.71; N 2.97.** Found: C 47.31; H 3.94; Br 34.82. Calc. for C₁₈H₁₈Br₂ClNO: C 47.00; H 3.96; Br 34.81.

procedure from suitably substituted benzophenones. The preparation of 9-allylidene-fluorene is given as a typical example in Fig. 2.

The side chain is attached by the Grignard procedure using γ -dimethylamino-propylmagnesium chloride as described by Marxer⁵ and Bonvincio *et al.*⁶ A reaction period of 6 h was used to ensure maximal conversion of the phenones, since some of these were rather insoluble. The Grignard reagent also is of limited solubility in ether and therefore used as a suspension. The benzhydryl derivatives obtained in this reaction were recrystallized from alcohol and melting points are presented in Table 1. The compounds were not analysed and the crude products were used in the following reaction.

Dehydration of the benzhydrol-bases was effected by treatment at reflux temperature with a mixture of hydrochloric and glacial acetic acid. The dimethyldiarylbutenylamines were oils or low-melting solids and were converted to the hydrochlorides. Melting points and analytical data are given in Table 1. The methiodides were prepared by treating an alcoholic solution of the free amine with an excess of methyl iodide; the crude product was used in the following reaction.

The elimination of amine from the methiodides was feasible by treatment with various basic reagents, but the most suitable procedure was found to consist in heating the salt with an alcoholic solution of sodium hydroxide (*cf.* Experimental). With the exception of two, all the diarylbutadienes could be crystallized from methanol.

The γ -dimethylaminopropylidene-2-chlorothioxanthene was separated into the *cis* and *trans* isomers as reported.⁷ By amine elimination from the quaternary amines, yielding the corresponding *cis* and *trans* butadienes, the configuration at the central double bond was retained.

Melting points of the 1,1-diaryl-1,3-butadienes, their analytical data and ultraviolet absorption bands are given in Table 2.

The butadienes, which are colourless or pale yellow, are very labile compounds which polymerize at elevated temperatures. They are also very sensitive to atmospheric oxygen. In order to obtain samples for analysis it was necessary to dry the material *in vacuo* after recrystallization and to avoid any contact with air by sealing the samples in an ampoule while under vacuum. The very fast oxygen uptake by some of the compounds was the cause of minor discrepancies in the analytical data.

The nature of the oxidation reaction is not known. In some cases formaldehyde is produced and usually the butadienes develop a yellow colour when exposed to the atmosphere. Kept *in vacuo* the compounds were stable for several months.

The ultraviolet absorption spectra of the compounds were recorded in the Cary Type 14 spectrophotometer using an 0.04 mM solution in cyclohexane. Wavelengths λ and molar extinction coefficient ϵ of the most characteristic absorption maxima are given in Table 2.

A strong absorption maximum at 287 $m\mu$, $\epsilon = 23\,400$, and a weaker at 236 $m\mu$, $\epsilon = 15\,800$, was observed for the unsubstituted 1,1-diphenyl-1,3-butadiene. Substitution at the *p,p'*-positions with halogen or alkyl led to bathochromic shifts and increase in intensity of both bands caused by the slight mesomeric interaction of these substituents with the conjugated system. Maximum effect was caused by bromine ($\lambda_{\max} = 294\,m\mu$, $\epsilon = 22\,000$). Substitution with methoxy groups at the *p,p'*-positions led to greater shifts ($\lambda_{\max} = 297.5\,m\mu$, $\epsilon = 20\,600$) while bis-dimethylamino substitution caused the greatest shift ($\lambda_{\max} = 317\,m\mu$, $\epsilon = 32\,000$).

The introduction of an *o,o'*-dimethylene bridge between the benzene rings (IV, R = H) caused a hypsochromic shift ($\lambda_{\max} = 270\,m\mu$) of the long wavelength band, which may be explained by the prevention of coplanarity because of the steric strain in the 7-membered ring. Introduction of bromine in this compound at the two positions *meta* to the central carbon (IV, R = Br) did not shift the 270 $m\mu$ absorption band.

Table 2. 1,1-Diaryl-1,3-butadienes. Roman numerals refer to Fig. 1.

Substituent R	M.p. °C	Formula	C		H		Halogen or N		Ultraviolet absorption bands							
			Found	Calc.	Found	Calc.	Found	Calc.	λ	ϵ	λ	ϵ	λ	ϵ		
			m μ	m μ	m μ	m μ	m μ	m μ	m μ	m μ	m μ	m μ	m μ	m μ	m μ	m μ
I H	35-37	C ₁₆ H ₁₄	92.96	93.16	6.90	6.84			287	23 400	236 ⁴	15 800				
I F	8-9	C ₁₆ H ₁₂ F ₂	79.32	79.31	5.25	5.00										
I Cl	49-50	C ₁₆ H ₁₂ Cl ₂	68.97	69.82	4.47	4.36	25.84	25.82								
I Br	72-74	C ₁₆ H ₁₂ Br ₂	52.07	52.73	3.40	3.32	43.60	43.94	294	26 900	256	22 000				
I CH ₃	50-52	C ₁₆ H ₁₆	92.10	92.31	7.92	7.69			292	27 700	246	19 500				
I (CH ₃) ₃ C	72-74	C ₂₄ H ₃₀	90.40	90.57	9.33	9.43			293	24 800	248	18 000				
I CH ₃ O	41-43	C ₁₈ H ₁₈ O ₂	81.77	81.14	6.87	6.84			297	20 600	258	15 100				
I (CH ₃) ₂ N	105-106	C ₂₀ H ₂₄ N ₂	81.60	82.20	8.15	8.22	9.62	9.58	317	32 200	266	S	232	20 000		
II H	71-72	C ₁₆ H ₁₂	93.35	94.12	6.26	5.88			339 ¹	19 300	268 ²	22 500	237	22 400	230	S
III H	71-72	C ₁₆ H ₁₂	91.27	92.61	7.28	7.39			297	23 900	227 ³	16 800				
IV H	58-59	C ₁₈ H ₁₆	92.40	93.10	7.22	6.90			271	22 100						
IV Br	128-130	C ₁₈ H ₁₄ Br ₂	54.20	55.37	3.64	3.61	40.52	41.02	270	18 400	216	29 300				
V H	59-61	C ₁₈ H ₁₄	93.75	93.90	6.23	6.08			311	S	273	23 500	261	24 300	239	35 300
VI H	oil	C ₁₆ H ₁₀ O	87.82	87.23	5.52	5.50			343	10 200	282	8 400	236	S	224	30 000
VI Br	114-115	C ₁₆ H ₁₀ Br ₂ O	50.40	50.79	2.75	2.65	41.70	42.33	354	13 800	277	13 700	234	60 000		
VII H	oil	C ₁₆ H ₁₂ S	80.37	81.32	5.27	5.12			345	6 700	287	16 500	240	27 200	220	15 600
VIII <i>trans</i>	70-72	C ₁₆ H ₁₁ SCI	70.35	70.95	4.15	4.10	12.89	13.12	350	7 500	288	21 800	242	37 900	214	29 000
VIII <i>cis</i>	94-96	C ₁₆ H ₁₁ SCI	69.42	70.95	4.22	4.10	13.07	13.12	350	7 600	287	22 200	241	38 000	214	32 000

¹ Additional peaks at 324 310, 297 and 284 m μ ² » » 257 and 247 m μ ³ » » 244 and 235 m μ ⁴ » » 230 and 223 m μ

In contrast to the effect of hindered coplanarity the fusion of the benzene rings into a planar system as in 9,9-dimethyl-9,10-dihydroanthracene (III) resulted in increased conjugation and a shift to $\lambda_{\max} = 297 \text{ m}\mu$. Ring fusion with oxygen or sulphur (VI, VII, VIII, and IX) gave rise to absorption at 345–349 $\text{m}\mu$, probably corresponding to the $n \rightarrow \pi^*$ transition of the electrons of the hetero atom.

The ultraviolet spectra of the *cis* and *trans* 9-allylidene-2-chlorothioxanthene (VIII and IX) were coinciding although their infrared spectra, taken on a Perkin Elmer "Infracord 137" spectrograph, were distinctly different.

The ultraviolet spectrum of the 9-allylidene-fluorene (II) displayed a long wavelength band at $\lambda_{\max} = 330 \text{ m}\mu$ with pronounced vibrational structure, pointing to increased conjugation in this compound.

EXPERIMENTAL

γ -Dimethylaminopropylmagnesium chloride. The procedure of Marxer⁵ was followed with some modifications. Freshly distilled dimethylaminopropyl chloride (230 g, prepared from the hydrochloride) was dissolved in 2 l of dry ether. Magnesium turnings (48 g) were covered with dry ether and 5 ml of ethyl bromide were added. When the reaction subsided the ether solution was added in the course of 30 min. Stirring was started and continued for 6 h. A suspension of the insoluble Grignard reagent was obtained. The concentration was found by titration to be 0.7 M. The suspension was kept in filled and well stoppered bottles.

Ketones. The benzophenones were prepared by Friedel–Crafts reaction according to the described procedure.⁸ Fluorenone was obtained by oxidation of fluorene.⁹ 10,10-Dimethylanthrone was prepared by methylation of anthrone with methyl iodide according to Hallgarten.¹⁰ Dibenzocycloheptadienone and dibenzocycloheptatrienone were prepared according to Campbell *et al.*¹¹ 2,7-Dibromodibenzocycloheptadienone was prepared by adding to 10 g of the parent ketone, 8 ml of bromine, and 100 mg of iron powder. After standing for one week at room temperature the excess bromine was removed with sodium hydroxide solution. The oil was crystallized from acetone to yield 3 g of product, m.p. 150°–155°. A sample was recrystallized for analysis from alcohol, benzene, and acetone, m.p. 160°–161°. (Found: C 48.60; H 2.60. Calc. for $\text{C}_{15}\text{H}_{10}\text{Br}_2\text{O}$: C 49.17; H 2.76). Thioxanthone and 2-chlorothioxanthone were prepared by the method of Prescott and Smiles.¹² Xanthone and 2,7-dibromoxanthone were prepared according to Dhar.¹³

4-Dimethylamino-1,1-diaryl-1-butanols. To 150 ml of the above mentioned suspension of γ -dimethylaminopropylmagnesium chloride was added with stirring 0.05 moles of dry ethyl ether. The mixture was stirred and heated to reflux for 6 h. After cooling, 200 ml of 1 M acetic acid was added with stirring. The ether layer was discarded and the water solution was neutralized to pH = 8.5 with ammonia. The mixture was extracted with 150 ml of chloroform and the chloroform layer was isolated and dried with potassium carbonate. Upon evaporation of the chloroform and cooling the product crystallized. A sample was recrystallized from ethyl alcohol for melting point determination. Yields of crude products were between 50 % and 90 %.

N,N-Dimethyl-4,4-diaryl-3-butenylamines. 5 g of the crude 4-dimethylamino-1,1-diaryl-1-butanol obtained above was refluxed for 1 h, dissolved in 20 ml of a 1:3 mixture of concentrated hydrochloric acid and glacial acetic acid. The mixture was cooled and made alkaline by addition of 30 % sodium hydroxide solution. The mixture was transferred to a separatory funnel and extracted with an equal volume of ether. The ethereal layer was separated, dried with potassium carbonate and the ether was evaporated. The resulting syrup was dissolved in 20 ml of acetone and a solution of hydrogen chloride in ether was added in an equimolar amount. By cooling and scratching, crystals of the hydrochloride were obtained which were isolated by filtration. A sample was purified for analysis and melting point determination by repeated recrystallization from ethyl alcohol. Yields above 80 % were obtained of the crude product.

Methiodides. Methiodides of the N,N-dimethyl-4,4-diaryl-3-butenylamines were prepared by converting 5 g of the hydrochloride to the free base, dissolving the base in 15 ml of alcohol, and adding 3 g of methyl iodide. After standing over-night the crystals were isolated, washed with ethyl ether, and dried. The yield was quantitative.

1,1-Diaryl-1,3-butadienes. To a mixture of 20 ml of ethyl alcohol and 2 ml of 30 % sodium hydroxide solution was added 2 g of the corresponding methiodide. The stirred mixture was heated to boiling for 3 min. Trimethylamine was evolved and the methiodide dissolved. The solution was cooled and diluted with 200 ml of water. An oil separated which was extracted with 50 ml of petroleum ether. The organic layer was separated and dried with anhydrous potassium carbonate. After evaporation of the solvent the residual oil was dissolved in 10 ml of methanol. The solution was treated with decolorizing carbon and filtered. When the flask was scratched and left in the refrigerator at -12° the product crystallized. The crystals were collected by filtration and washed with cold methanol. The product was transferred to an ampoule and dried under vacuum. The yields of pure product varied from 50 % to 90 %.

Microanalyses were performed by Mr. Preben Hansen, Microanalytical Division, The Chemical Laboratory, The University of Copenhagen. The author wishes to thank Professor N. Hofman-Bang for the use of a Cary spectrophotometer. Infrared spectra were determined by Mrs. I. G. Krogh Andersen of this laboratory.

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