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A Novel Method for the Synthesis of Triphenylenes

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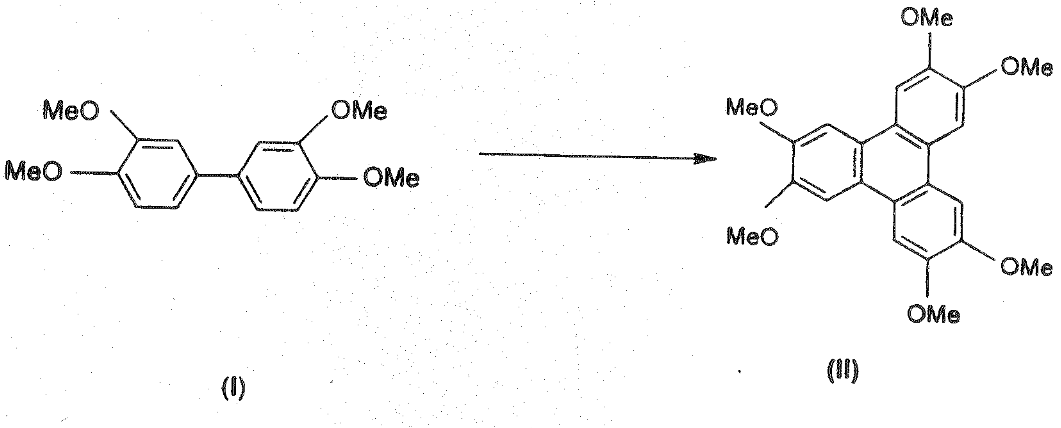
A novel method is described for the synthesis of triphenylenes, which involves the coupling of 1,2-diiodobenzenes using copper bronze. Many compounds were synthesized using this method.

Key Words: Synthesis, Triphenylene, Liquid crystals.

INTRODUCTION

Until now, studies on triphenylene liquid crystals have been limited to hexasubstituted derivatives of triphenylene. This is because only one feasible method for the synthesis of substituted triphenylene (II) has been reported[1].

The reaction involves the treatment of 3,4,3′,4′-tetramethoxy biphenyl (I) and veratrole with chloranil in aq. sulphuric acid (Scheme-I). This method ensures only one product is obtained. The uses of disubstituted biphenyls were difficult to separate.

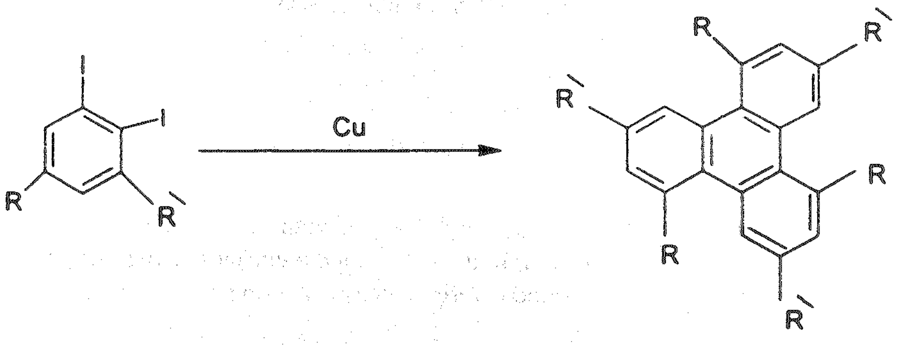


Scheme-I

It would be of interest for liquid crystal studies to synthesize triphenylene possessing other substitution pattern.

McOmie *et al.*[2] and Corbett *et al.*[3] studied the reaction between the substituted diiodobenzene with copper bronze; they obtained substituted biphenylene in 5–40% yields. Work in the field of biphenylene synthesis led to this novel method for the synthesis of triphenylenes, which involves the coupling of 1,2-diiodobenzene with copper bronze.

The first precursors targeted for this purpose were the diiodides (**IIIa–c**). The triphenylenes (**IVa–c**) were obtained using this method (**Scheme-II**).



(III) (IV)

where	**IIIa**	$R = NO_2$	$R' = H$
	IIIb	$R = CO_2Me$	$R' = H$
	IIIc	$R = NO_2$	$R' = CH_3$

Scheme-II

EXPERIMENTAL

Melting points were determined on an electrothermal melting point apparatus and are uncorrected. ^1H NMR spectra were obtained on JEOL GX 270 and 400 spectrometers; samples were run as solution in $CDCl_3$ at ambient temperature and chemical shifts are recorded in ppm downfield from internal tetramethylsilane. Mass spectra were obtained on an AEI MS903 instrument operated at 70 eV and a source temperature of 200°C. Infrared spectra were obtained by using Perkin-Elmer 237 infrared spectrometer in KBr discs.

Preparation of 2,3-diiodonitrobenzene (IIIa)

2-iodo-6-nitroaniline (10 g) in glacial acetic acid (75 mL) was added with strring to sodium nitrite (3 g) in concentrated sulphuric acid (50 mL). The temperature was kept below 10°C. The reaction mixture was added to KI (10 g) in water (100 mL). The resulting mixture was heated over a steam bath for 60 min. Then cold water (100 mL) was added to the mixture, finally the product was extracted with ether. On evaporating the solvent, the crude product was recrystallized from methanol as brown needles (11.0 g, 78%), m.p. 120–122°C (Lit.[4] 122–124°C).

Methyl-2-3-diiodobenzoate (IIIb)

The compound was prepared using the method described by Newman[4]; the diiodide (**IIIb**) was obtained as colourless crystals, m.p. 48–50°C.

3,4-Diiodo-5-nitrotoluene (IIIc)

The compound (**IIIc**) was prepared from 4-amino-3-nitro-5-iodotoluene using the same method as used for the preparation of (**IIIa**); it was obtained in 71% yield as yellow crystals, m.p. 58–60°C. ^1H NMR ($CDCl_3$): δ/ppm 7.20–7.95 (d, 2H, aromatic), 2.25 (s, 3H, CH_2).

General method for the synthesis of compounds (IVa–c)

The diiodide (III) (0.03 mol) in acetone (10 mL), acetonitrile (10 mL) and aqueous ammonia (5 mL) was kept at room temperature. To this mixture copper bronze (0.09 mol) was added with stirring. The stirring was continued at this temperature for 8–18 h. The resulting mixture was poured into a saturated solution of sodium chloride (50 mL). The solvent was evaporated *in vacuo,* the residue was washed with water and then it was extracted with chloroform, which was dried over magnesium sulphate. On evaporating the solvent, the crude product was recystallized from ethanol. The following compounds were synthesized using this method.

1,5,9-Trinitrotiphenylene (IVa)

^{1}H NMR ($CDCl_3$): δ/ppm 7.65 (q, Hc), 7.95 (d, Hb) and 8.50 (d, Ha). IR (cm^{-1}): 1480 ν(NO_2).

Trimethyl-1,5,9-Triphenylenetricarboxylate (IVb)

^{1}H NMR ($CDCl_3$): δ/ppm 7.48 (q, Hc), 7.80 (d, Hb) and 8.10 (d, Ha) and 3.85 (s, CH_3CH_3COOH); IR (cm^{-1}): 1750 ν(C═O).

3,7,11-Trimethyl-1,5,9-Trinitrotriphenylene (IVc)

^{1}H NMR ($CDCl_3$): δ/ppm 7.62 (q, Hc), 7.82 (d, Hb) and 2.60 (s, q, CH_3). IR (cm^{-1}): 1450 ν(NO_2).

RESULTS AND DISCUSSION

In the present work, the compounds (**IIIa–c**) react with copper bronze at room temperature with continuous stirring for 8 h for di-iodides (**IIIa–b**) and for 18 h for compound (**IIIc**).

The triphenylenes (IVa–c) were obtained in moderate yields (Table-1). Structural assignment of the resulting triphenylens (**IVa–c**) are based on elemental analysis and spectral data. The ^{1}H NMR of **IVa** shows doublets for the proton Ha ($\delta = 8.20$ ppm) and Hb ($\delta = 7.95$ ppm). It shows double doublet for Hc ($\delta = 7.65$ ppm) (Fig. 1). The IR specta exhibit one ν(NO_2) stretching frequency at 1480 cm^{-1}. The electron impact (EI) spectrum of this compound displays the correct molecular ion in accordance with the suggested molecular formula. It showed a molecular ion at 368 m.u. (80%), which fragmented to give parent ion 287 m.u. (100%).

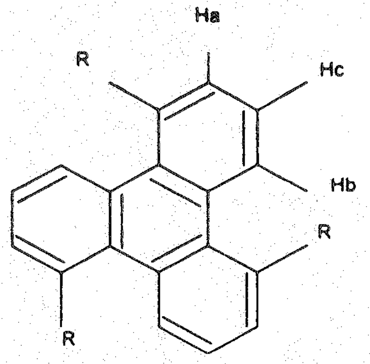


Fig. 1

TABLE-1
PHYSICAL AND ANALYTICAL DATA OF COMPOUNDS (**IVa–c**) AND FOR (**IIIc**)

Compound No.	Yield (%)	Colour	m.p. (°C)	m.f. (m.w.)	% Analysis, Found (Calcd.)		
					C	H	N
IIIc	28	Pale yellow crystals	304–306	$C_{18}H_9N_3O_6$ (363)	59.45 (59.51)	2.45 (2.50)	11.25 (11.65)
IVa	71	Yellow	58–60	$C_7H_5N_2O_2$ (389)	21.62 (21.86)	1.30 (1.28)	3.60 (3.41)
IVb	24	White crystals	158–160	$C_{24}H_{18}O_6$ (402)	71.43 (71.64)	4.62 (4.51)	—
IVc	20	White crystals	300–304	$C_{21}H_{15}N_3O_6$ (405)	62.04 (62.22)	3.59 (3.73)	10.18 (10.36)

The triphenylene (**IVb**) was obtained as a white crystalline solid after leaving the reaction mixture under stirring for 8 h. ^{1}H NMR spectrum showed doublets for the protons Hb ($\delta = 7380$ ppm) and Ha ($\delta = 8.10$ ppm); it showed a quartet for Hc ($\delta = 7.84$ ppm) and singlet for the CH_3 protons of CH_3COO at ($\delta = 3.85$ ppm). The mass spectrum showed a molecular ion at 402 m.u. (100%). The IR spectrum of (**IVb**) exhibited strong absorption band at 1720 cm^{-1} ν(C=O).

The triphenylene (**IVc**) was obtained after stirring the reaction mixture for 8 h. The ^{1}H NMR spectrum of this compound showed singlets for the proton Ha ($\delta = 7.82$ ppm) and Hb ($\delta = 7.62$ ppm); also it showed a singlet for the protons of CH_3 at $\delta = 2.60$ ppm.

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