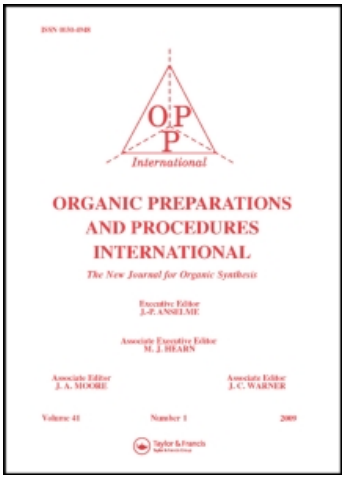

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SYNTHESIS OF NEW BIS-DIPHENYLACETYLENES

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SYNTHESIS OF NEW BIS-DIPHENYLACETYLENES

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Although Diels-Alder reactions of dienes with diethynylic dienophiles have been used[1,2] to prepare phenyl substituted polyphenylenes, this useful method of synthesizing polymers containing controlled aromatic backbone segments has suffered from the limited availability of bis-diacetylenes.[3-22] With the exception of the method of Hay[12] which affords meta- and para-diethynylbenzenes in reasonable yields, the other diethynylbenzenes available are prepared in low yields using multistep reactions.[3-11,13-22]

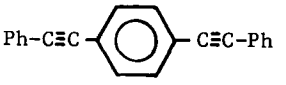
We now report the one-step preparation of a new class of diethynylic compounds in high yields. The reaction of benzil or substituted benzils with an excess of triethyl phosphite has been reported to afford a 1:1 adduct which could then be converted to a diphenylacetylene when pyrolyzed in the presence of excess triethyl phosphite.[23] Modification of this

$$Ar\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}Ar \;+\; (C_2H_5O)_3P \xrightarrow{215^\circ} Ar\text{-}C{\equiv}C\text{-}Ar$$

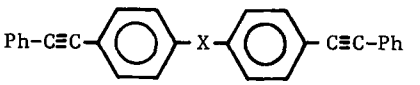
procedure by reaction of 4-phenylglyoxalylbenzil (I),[24] 4,4'-diphenylglyoxalylbiphenyl (II),[25] 4,4'-diphenylglyoxalyldiphenylmethane (III),[25] 4-phenylglyoxalylphenyl ether (IV),[25] or 4-phenylglyoxalylphenyl sulfide (V)[25] with an excess of triethyl phosphite in a Carius tube sealed under an inert nitrogen atmosphere and heated in a Wood's Metal bath for varying periods at 215°, afforded the corresponding diethynylic compounds in

good yields (Table I).

Table I. Physical Data For Bis-diphenylacetylenes.[a]



VI



X = nil VII X = O IX

X = CH_2 VIII X = S X

Bis-diphenylacetylenes	Yield (%)	mp. (°C)	Formula	Elemental Analysis % Calculated (% Found) C	H
1,4-bis(phenylethynyl)-benzene (VI)[b]	80	182-183[c]	$C_{22}H_{14}$	94.93 (94.66)	5.07 (4.87)
4,4'-bis(phenylethynyl)-biphenyl (VII)[b]	82	219-220	$C_{28}H_{18}$	94.88 (94.80)	5.12 (5.10)
4,4'-bis(phenylethynyl)-diphenylmethane (VIII)	74	130.5-131	$C_{29}H_{20}$	94.53 (94.25)	5.47 (5.52)
4,4'-bis(phenylethynyl)-diphenyl ether (IX)	80	184-185	$C_{28}H_{18}O$	90.78 (90.99)	4.90 (4.95)
4,4'-bis(phenylethynyl)-diphenyl sulfide (X)	84	206-207	$C_{28}H_{18}S$	87.01 (87.17)	4.69 (4.74)

[a]Reaction time was 7 hrs unless otherwise noted. [b]Reaction time: 24 hrs. [c]Lit. mp. 181-182°;[10] 184-186°.[9]

The availability of the bis-diphenylacetylenes VII-X now makes it possible to introduce greater flexibility into Diels-Alder polyphenylene polymers through the diethynylic dienophiles, whereas previously this could only be done through the structure of the dienes.

EXPERIMENTAL

General Procedure.- Into a Carius tube was placed 9.96 g (60.0 mmol) of freshly distilled triethyl phosphite (bp. 53-54°/14 mm) and 5.0 mmol of the respective benzil (I-V). After bubbling nitrogen through the solution for 10 min, the Carius tube was sealed, placed in a Wood's Metal bath and heated at 215°. After 7 hrs, the tube was cooled to room temperature and opened *cautiously*. (Pressure is built up in the tube). The excess triethyl phosphite was removed from the reaction mixture by distillation under reduced pressure and the resulting semi-solid was recrystallized three times from 25 ml portions of absolute ethanol. The yields and melting points of the bis-diphenylacetylenes obtained are reported in Table I.

1,4-Bis(phenylethynyl)benzene (VI).- The reaction time for the preparation of this bis-diphenylacetylene was 24 hrs. The product precipitated from the reaction mixture in the Carius tube and was collected and then recrystallized. Concentration of the triethyl phosphite by distillation under reduced pressure did not afford any additional product.

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