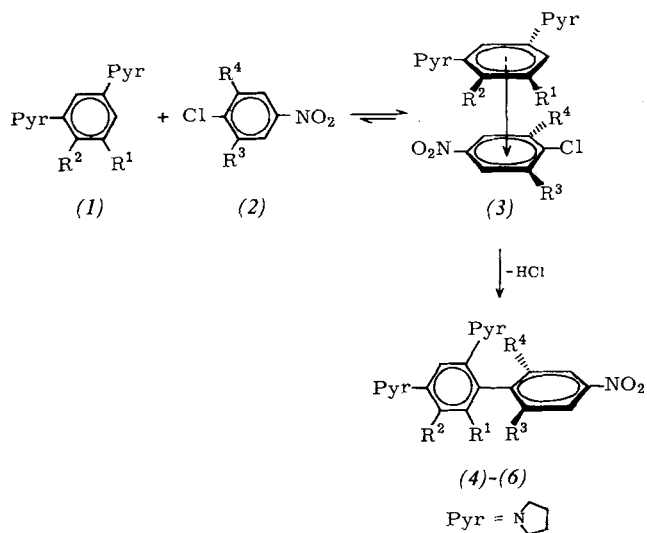


## Nucleophilic Aromatic Substitution: A New Synthetic Route to Biphenyls<sup>[1]</sup>

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The most important methods for preparation of biphenyls are the Ullmann<sup>[2]</sup> and G6mberg reactions<sup>[3]</sup>, which involve radical or organometallic intermediates; furthermore, biaryls are formed by benzidine rearrangement<sup>[4]</sup> and oxidative dimerization<sup>[5]</sup>, as well as in the course of reactions involving aryne intermediates<sup>[6]</sup>.



	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>
(4a)	Pyr	CH <sub>3</sub>	NO <sub>2</sub>	NO <sub>2</sub>
(5a)	Pyr	H	NO <sub>2</sub>	NO <sub>2</sub>
(5b)	Pyr	H	CN	NO <sub>2</sub>
(5c)	Pyr	H	COOCH <sub>3</sub>	NO <sub>2</sub>
(5d)	Pyr	H	COOH	NO <sub>2</sub>
(5e)	Pyr	H	H	NO <sub>2</sub>
(5f)	Pyr	H	H	CN
(6a)	H	H	NO <sub>2</sub>	NO <sub>2</sub>
(6b)	H	H	COOCH <sub>3</sub>	NO <sub>2</sub>

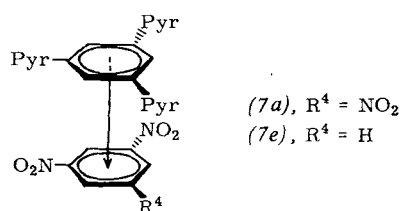
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By treating aminobenzenes (1) with reactive haloarenes (2), we have now obtained a polar aryl-aryl linkage via nucleophilic aromatic substitution, yielding biphenyl derivatives (4) to (6).

In all cases, closure of the new C—C bond is preceded by formation of charge-transfer (CT) complexes (3) which may be isolated in crystalline form if reaction conditions are kept sufficiently mild. Only when heated do the CT complexes lose HCl to give biphenyls (4) to (6) (Table 1). The reactivity of the components (1) and (2) may be varied within wide limits. When tripyrrolidinobenzene is treated with chlorotrinitrobenzene (2a) the reaction mixture begins to boil. Upon introduction of an alkyl group R<sup>2</sup> into the aminobenzene (1), the two *ortho* pyrrolidino rings are twisted out of the aromatic ring plane<sup>17, 81</sup>; reduced mesomeric interaction results in a decrease in electron density and thus also in the reactivity at the free ring positions. Consequently, heating is required for reaction of 1-methyl-2,4,6-tripyrrolidinobenzene with (2a); with 1-ethyl-2,4,6-tripyrrolidinobenzene, the reaction does not proceed beyond the CT complex stage. For the haloarenes, 2-chloro-4-nitrobenzoic acid represents about the limit of reactivity towards tripyrrolidinobenzene.

The structure of the new biaryls is established by elemental analyses, molecular-weight determinations, and NMR spectra. Unexpectedly, compounds (4) to (6) are obtained as dark red to black, shiny crystals; from position, intensity, and structure of the visible absorption bands which determine the color (Table 1), interpretation as charge-transfer transitions is rather likely. Intermolecular CT interaction can be ruled out since Lambert-Beer's law holds unambiguously even at low concentrations. For a check, we have prepared comparable CT complexes (7), which, as expected, show increasing dissociation as the concentration is lowered.

The geometry of the biphenyls (4) to (6) is fixed to a large extent, thus allowing a more detailed study of the intramolecular charge transfer on which we report in the accompanying Communication<sup>19</sup>.



Lowest-energy absorption of (7a) (630 nm in CH<sub>2</sub>Cl<sub>2</sub>)

<i>c</i>	$7 \times 10^{-3}$	$7 \times 10^{-4}$	$7 \times 10^{-5}$
<i>d</i>	0.1 cm	1.0 cm	10.0 cm
<i>E</i>	0.31	0.05	ca. 0.01

Table 1. Biphenyls (4) to (6) obtained from aminobenzenes (1) and chlorobenzenes (2).

	Yield (%)	M. p. (°C)	$\lambda_{\max}$ (nm); $\epsilon_{i, \max}$ in CH <sub>2</sub> Cl <sub>2</sub>	
(4a)	78	189–190	572.5; (3860)	424.5; (4870)
(5a)	79	174–176	587 ; (6300)	414 ; (3560)
(5b)	76	203	560 ; (6140)	416 ; (2180)
(5c)	57	186	549 ; (5700)	sh
(5d)	59	198	ca. 535 ; (sh)	426.5
(5e)	85	209–210	524.5; (6690)	395 ; (2650)
(5f)	64	212	484.5; (5680)	405 ; (1440)
(6a)	77	179	563 ; (6820)	427 ; (3200)
(6b)	84	148	523 ; (6650)	sh

Methyl 2,4-dinitro-2',4'-dipyrrolidino-6-biphenylcarboxylate (6b):

Methyl 2-chloro-3,5-dinitrobenzoate (2c) (3.66 g, 0.016 mol) in solution in ethanol (15 ml) is added to 1,3-dipyrrolidinobenzene (6.48 g, 0.03 mol) in CHCl<sub>3</sub> (15 ml). The mixture, which at once turns dark red, is briefly boiled and then treated with ethanol (50 ml). On cooling, almost black crystals of the CT complex (3) deposit (R<sup>1</sup>=R<sup>2</sup>=H, R<sup>3</sup>=COOCH<sub>3</sub>, R<sup>4</sup>=NO<sub>2</sub>) (84%), m. p. 79°C,  $\lambda_{\max}$  = 537 nm (*E* = 0.27;  $3.3 \times 10^{-3}$  M in CH<sub>2</sub>Cl<sub>2</sub>). Complex (3) is redissolved in the mother-liquor by warming and heated under reflux for 4 h. After cooling, the biphenyl (6b) is precipitated in dark red crystals; it can be recrystallized from ethanol-light petroleum.

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[2] R. G. R. Bacon and H. A. O. Hill, *Quart. Rev.* 19, 95 (1965).

[3] W. E. Bachmann and R. A. Hoffman, *Org. Reactions* 2, 224 (1944).

[4] H. J. Shine in B. S. Thyagarajan: *Mechanisms of Molecular Migrations*. Interscience, New York 1969, p. 191.

[5] R. N. Adams, *Accounts Chem. Res.* 2, 175 (1969), and literature cited therein; E. C. Taylor, F. Kienzle, and A. McKillop, *J. Amer. Chem. Soc.* 92, 6088 (1970).

[6] R. W. Hoffmann: *Dehydrobenzene*. Verlag Chemie, Weinheim 1967, p. 106.

[7] W. Schoeller, *Dissertation*, Universität Stuttgart 1969; W. D. Stohrer, *Dissertation*, Universität Stuttgart 1969.

[8] F. Effenberger, E. Auer, and P. Fischer, *Chem. Ber.* 103, 1440 (1970).

[9] E. Daltrozzo, F. Effenberger, and P. Fischer, *Angew. Chem.* 83, 621 (1971); *Angew. Chem. internat. Edit.* 10, 567 (1971).