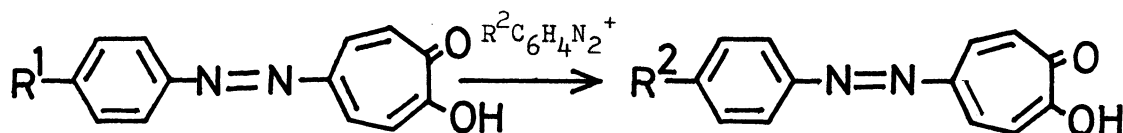


ARYLAZO GROUP EXCHANGE IN THE REACTION OF
5-ARYLAZOTROPOLONES WITH ARYLDIAZONIUM SALTS

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5-Phenylazo-, 5-(p-tolylazo)-, and 5-(p-methoxyphenylazo)-
tropolones reacted with aryldiazonium salts to give products
which derived from arylazo group exchange at the C-5 position
of the tropolone ring.

Tropolones having no substituents at the C-5 position of the tropolone ring have
been reported to form nicely crystalline dyes by the diazo-coupling reaction.¹⁾ On
the other hand, little is known about the reaction of 5-substituted tropolones with
aryldiazonium salts except the following fact: Toda et al.²⁾ reported that a tropolone
substituted at the C-5 position with chlorine, isopropyl, methoxyl, or phenyl group
was treated with an aryldiazonium chloride to afford the corresponding 3-arylazotro-
pologes. In the course of our work to clarify the reaction of 5-substituted tro-
pologes with aryldiazonium salts, we found that 5-arylazotropolones react with aryl-
diazonium salts to give rise to arylazo group exchange reaction in aromatic compounds.



Ia $R^1 = H$
Ib $R^1 = CH_3$
Ic $R^1 = OCH_3$

IIa(≡Ia) $R^2 = H$
IIb $R^2 = Cl$
IIc $R^2 = Br$
IIId $R^2 = COOCH_3$
IIe $R^2 = COCH_3$
IIIf $R^2 = CN$
IIIg $R^2 = NO_2$

When tropolones substituted at the C-5 position with phenylazo, p-tolylazo, or
p-methoxyphenylazo group were treated with aryldiazonium chloride, having electron-
withdrawing groups at the para position, in pyridine at low temperature (-5 ~ -10°C),
the arylazo group exchanged products were obtained in 55-92% yields as shown in Table
1. These products were identified by their mp's and infrared spectra in comparison
with those of their authentic samples. However, when aryldiazonium salts having
electron-releasing substituents were used under the same conditions, the starting 5-
arylazotropolones were recovered.

Table 1. Yields of the Exchanged Products

Product	Yield (%) from			Mp (°C)	(in ref.)
	Ia	Ib	Ic		
IIa	—	#	61	160	(160-161) ³⁾
IIb	83	74	82	245	(244-245) ⁴⁾
IIc	92	80	86	253-254	(249-250) ⁵⁾
IId	60	55	70	243-244	##
IIe	81	90	63	243-245	(239-241) ⁴⁾
IIIf	92	76	62	271-272	(269-271) ⁴⁾
IIg	88	75	84	267-268	(249-250) ⁶⁾

No reaction.

A new compound gave satisfactory elemental analysis.

When substituents at the para position of arylazo group were electron-withdrawing ($R^1 = Cl$ and $COCH_3$), the arylazo group exchange did not occur. This finding clearly indicates that the reaction of 5-substituted tropolones with aryldiazonium salts depends largely on the electronic effect of the substituents at the C-5 position.

The details of the diazo-coupling reaction of 5-substituted tropolones will be reported later on.

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