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AZOCOUPLING REACTION OF 5-SUBSTITUTED TROPOLONES ----- THE FORMATION OF 3-ARYLAZOTROPOLONES

T. Toda, H. Horino (1), T. Mukai and T. Nozoe
Department of Chemistry, Faculty of Science,
Tohoku University, Sendai, Japan

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The azo-coupling reaction of tropolones usually occurs at the C-5 position of the tropolone ring with the formation of nicely crystalline dyes (2,3). On the other hand, tropolones having a substituents at the C-5 position have been reported to form amorphous pigments by the diazo-coupling reaction, but the properties and structures of the products have not been clarified (2a, 4). We wish to report here the formation of 3-arylazo-5-substituted tropolones, which is the first clear example of this type of azo-coupling reaction of troponoid compounds.

When a tropolone substituted at the C-5 position with chlorine, isopropyl, methoxyl or phenyl group was treated with an aryldiazonium chloride, having an electron-withdrawing group at the para position, in pyridine at low temperature (-5—-10° C), the corresponding 3-arylazotropolone (I-XI) was obtained in 24-63 % yield as shown in Table 1. However, when an aryldiazonium salt having an electron-releasing substituent was used under the same conditions, the 5-substituted tropolone was recovered unchanged. It should be noted that the yield of azo-dye was considerably lower in the case of 5-isopropyl- or 5-methoxytropolone.

The structure of 3-(nitrophenyl)azo-5-phenyltropolone (I) was proved by the reduction of I with sodium hydrosulfite affording 3-amino-5-phenyltropolone (5). The structure of other products obtained were confirmed analogously.

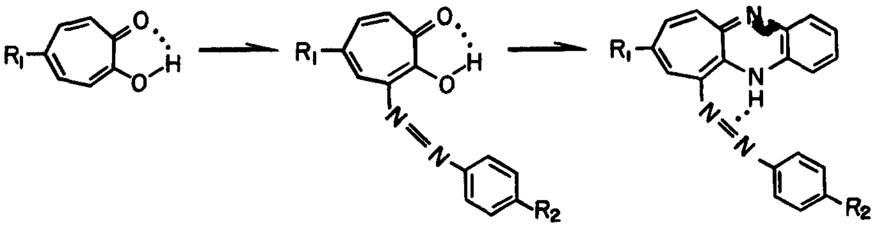


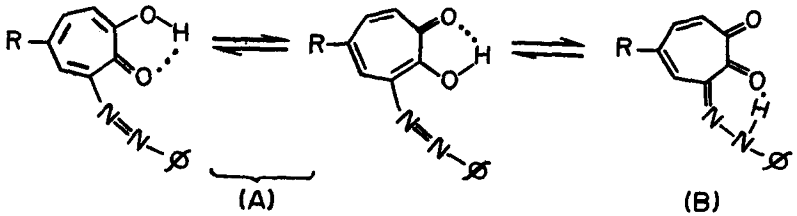
TABLE 1

Substituents		Azo compounds		Yield	Qunoxaline derivatives	
R_1	R_2	No	mp° C	%	No	mp° C
Ph	NO_2	I	214	41	XII	265
Ph	Cl	II	164	50	XIII	228
Ph	Br	III	162	42	XIV	234
Ph	COOMe	IV	117	63	XV	233
Ph	H	V	amorph.		XVI	172
Cl	NO_2	VI	213	56	XVII	213
Cl	Cl	VII	186	40	XVIII	232
Cl	Br	VIII	196	53	XIX	235
$i-C_3H_7$	NO_2	IX	171	23	XX	229
$i-C_3H_7$	Cl	X	183	25	XXI	142
OMe	Cl	XI	amorph.		XXII	202

These 3-arylazotropolones gave good crystalline quinoxaline derivatives (XII ~ XXII) when they were treated with o-phenylenediamine, as in the case of 5-arylazotropolones (6). These derivatives provided a good means of characterizing non-crystalline 3-azo compounds such as V or XI.

The 3-arylazotropolones absorb at longer wave lengths than do the corresponding 5-arylazotropolones. For example, I shows: λ_{max}^{MeOH}, mμ (log ε); 250 (4.24), 327 (4.32) and 460 (3.96). Although 5-arylazotropolones show a OH stretching absorption band near 3200 cm^{-1} and a strong band near 1620 cm^{-1} in their infrared spectra (7), 3-arylazotropolones show broad and rather weak bands near 3000 cm^{-1} and two bands with medium intensities near 1600 cm^{-1}.

It is possible that 3-arylazotropolones exist as an equilibrium mixture of the troponoid forms (A) and the quinonoid form (B). Actuallyl, 5-tolylazotropolone afforded a N-methyl derivative as well as an O-methyl derivative on methylation with diazomethane (7). However, methylation of II with diazomethane or methyl iodide gave only the two tropolone methyl ethers, one m.p. 116° and the other m.p. 141° C, but no N-methyl derivative. Both of them afforded the same quinoxaline derivative XIII in good yield by treatment with o-phenylenediamine.



The azo-coupling reaction of 5-halotropolones resulted in replacement of the halogen atom by the azo group and sometimes in the replacement plus resubstitution by the removed halogen atom. For instance, when treated with p-nitrophenyl diazonium salt, 5-bromotropolone afforded 3-bromo-5-(p-nitrophenyl)azotropolone m.p. 238° (8), whereas 5-iodotropolone gave 5-(p-nitrophenyl)azotropolone m.p. 275°, both products being obtained in good yield. It is not clear yet whether rearrangement of the bromine atom proceed by an intramolecular or intermolecular reaction. Analogous replacements of the 5-substituent in the tropolone ring by other cationoid reagents have been observed in the cases of 3- and 5-hydroxymethyl- (9), 5-morpholino- (10), and 3- and 5-tropyl-tropolones (11). Presumably, if such substituents are good leaving groups or form stable cations, this type of replacement will occur fairly easily.

Since it has been shown that azo-couplings can take place as either 3- or 5- position in the tropolone nucleous, it is clear that this reaction can no longer be considered as a reliable diagnostic test for 5-substituted tropolones.

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