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DIAZO-COUPLING REACTION OF 5-METHYLTROPOLONE. THE FORMATION OF 3,7-DIARYLAZOTROPOLONES

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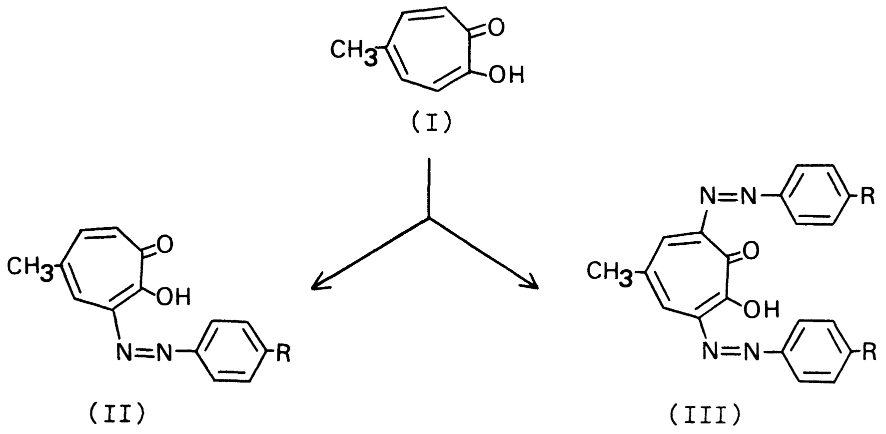
5-Methyltropolone reacted with aryldiazonium salts to give either 3-arylazo-5-methyltropolones or 3,7-diarylazo-5-methyltropolones according to the electrophilicity of the attacking species.

It is well known that tropolones having no substituent at the C-5 position give nicely crystalline 5-arylazotropolones by the diazo-coupling reaction.[1] In the case of 5-substituted tropolones, there are the following two examples with regard to the reactions with aryldiazonium salts. Firstly, a tropolone substituted at the C-5 position with chlorine, isopropyl, methoxyl, or phenyl group gave the corresponding 3-arylazotropolone when treated with an aryldiazonium salt.[2] Secondly, tropolones having hydroxymethyl,[3] morpholinomethyl,[4] tropyl,[5] bromine,[2] or iodine[2] at the C-5 position underwent replacement of the substituent with arylazo group. Now, we wish to report the third example, the formation of 3,7-diarylazotropolones (III), of diazo-coupling reaction of troponoid compounds, as shown in Scheme 1.



IIa R = H
IIb R = $COCH_3$
IIc R = CN

IIIa R = CH_3
IIIb R = Cl
IIIc R = Br

Scheme 1

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When 5-methyltropolone (I) was treated with p-acetylbenzenediazonium chloride having a strongly electron-withdrawing group at the para position, at low temperature ($-5\sim-10^{\circ}C$), 3-(p-acetylphenylazo)-5-methyltropolone (IIb) was obtained: yield 68%, mp 163°C; IR (KBr) 1700(C=O), 1595(C=O), 1555 cm^{-1}; NMR (CF_3COOH) δ 2.46(s, 3H, $COCH_3$), 2.66(s, 3H, CH_3), 7.29(s, 2H, H-4,6), 7.53(s, 1H, H-7), 7.93(d, 2H, H×2, J=9.2Hz), 8.13 (d, 2H, H×2, J=9.2Hz); found C 67.69, H 5.01, N 9.81%, calcd for $C_{16}H_{14}N_2O_3$ C 68.07, H 5.00, N 9.92%; quinoxaline derivative, mp 272°C. The reaction with p-cyanobenzenediazonium salt gave also a 3-arylazotropolone derivative (IIc): yield 71%, mp 182°C.

On the other hand, when p-tolyldiazonium salt was used under the same condition, 3,7-diarylazo-5-methyltropolone (IIIa) was obtained: yield 15%, mp 183°C; IR (KBr) 1602(C=O), 1545 cm^{-1}; NMR (CF_3COOH) δ 2.67(s, 6H, CH_3×2), 2.76(s, 3H, CH_3), 7.55(d, 4H, H×4, J=7.8Hz), 7.97(d, 4H, H×4, J=7.8Hz), 8.56(s, 2H, H-4,6); found C 70.57, H 5.48, N 14.53%, calcd for $C_{22}H_{20}N_4O_2$ C 70.95, H 5.41, N 15.05%; quinoxaline derivative, mp 183°C. The reaction of an aryldiazonium salt having a weakly electron-withdrawing (Cl or Br) substituent gave also 3,7-diarylazo-5-methyltropolone (III): IIIb, yield 63%, mp 205°C; IIIc, yield 72%, mp 207°C.

In addition, the reaction with benzenediazonium chloride yielded a tarry material which gave a quinoxaline derivative (mp 172°C, 38%) of the form (II) with o-phenylenediamine. The structure of all the products was confirmed by their spectral data and elemental analyses.

To summarize, the reaction seems to depend on both the substituent at the C-5 position and the electrophilicity of the attacking species. The details will be reported in the near future.

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References

1) T. Nozoe, K. Takase, and H. Matsumura, "Dai Yuki Kagaku," ed. by M. Kotake, Vol. 13, Asakura Shoten, Tokyo (1960), p. 281.
2) T. Toda, H. Horino, T. Mukai, and T. Nozoe, Tetrahedron Lett., 1968, 2387.
3) S. Seto and K. Ogura, Bull. Chem. Soc. Jpn., 32, 493 (1959).
4) K. Ogura, Bull. Chem. Soc. Jpn., 34, 839 (1961).
5) T. Nozoe, T. Tezuka, and T. Mukai, Bull. Chem. Soc. Jpn., 36, 1470 (1963).

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