Auwers's 2-Hydroxy-3-arylindazoles: a Structure Revision

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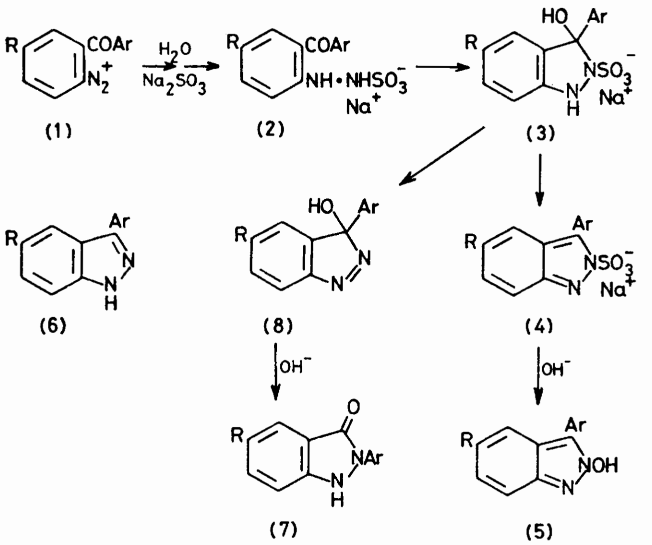
Summary The title compounds are shown by ^{13}C and ^{15}N n.m.r. and u.v. spectroscopy to be 3-aryl-3-hydroxy-3*H*-indazoles.

Although the literature on 2-hydroxyindazoles is sparse,[1] some half-dozen examples have been reported. The parent compound[2] and one other[3] have been made by decomposition of *o*-azidobenzaldoximes; the remainder, which all carry a 3-aryl substituent, are formed by the action of sodium sulphite on diazotized *o*-aminobenzophenones (**1**), a procedure first described by Auwers.[4] These 3-aryl compounds, to which structure (**5**) was assigned, are unstable, decomposing thermally to give the benzophenones, and rearranging in hot alkali to form 2-aryl-3-indazolinones (**7**).[4] They can be reduced ($SnCl_2$) to the 3-arylindazoles (**6**).[4] Recently Kametani *et al.*[5] exploited the reaction as a route to the indazolinones (**7**), and they proposed a scheme (**1**)→(**2**)→(**3**)→(**4**)→(**5**) for the formation of the *N*-hydroxy compounds, largely following Auwers's original suggestions. In our opinion the final step is an implausible one; the *N*-sulphonyl compounds (**4**) would rather be desulphonated, to form the indazoles (**6**), which are reported as by-products in the reaction, and 3-methylindazole is the main product of the corresponding reaction starting from *o*-aminoacetophenone.[4]



The chemical properties of the products, and particularly their instability and weak acidity, contrast strongly with those of a number of 3-unsubstituted 2-hydroxy- and -alkoxy-indazoles recently prepared in this laboratory.[6] Furthermore, the mass spectra of these latter compounds show strong parent ions (M^+), while in those of Auwers's compounds (Ar = Ph, R = H, and some other derivatives) the M^+ ion is barely perceptible, the most prominent heavy ions arising from $(M - OH)^+$ and $(M - N_2)^+$. We considered that the structure (**8**) better explained the chemistry of these aryl derivatives, and have found evidence for the presence of the azo-grouping in the u.v. (λ_{max} 380, ϵ 150) and ^{15}N n.m.r. (screening constants −121 and −76 p.p.m., relative to $MeNO_2$)† spectra of the 5-chloro-3-phenyl compound. In the ^{13}C n.m.r. spectrum, the unusual environment of C(3) brings it far down-field, to 113·8 p.p.m. (in dioxan; $Me_4Si = 0$). This agrees well with the C(3) shifts (*ca.* 118 p.p.m.) of a series of 3-aroyloxy-3,5,5-trimethyl-1-pyrazolines, which have recently been reported.[7] Other compounds prepared similarly have been examined, and all show spectra in agreement with structure (**8**).

The chemical properties of these compounds, which are loosely protected aryldiazenes, are being investigated further, and work is presently being carried out on chemical means of distinguishing between structures (**5**) and (**8**), and also on authentic 2-hydroxyindazoles.

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† Azole and azine nitrogen atoms usually resonate upfield of nitromethane; cinnoline provides a significant exception (M. Witanowski, L. Stefaniak, and H. Januszewski, in 'Nitrogen NMR,' eds. M. Witanowski and G. A. Webb, Plenum Press, London and New York, 1973, Ch. 4).

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