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COMPETITIVE PATHWAYS IN THE REACTION BETWEEN AROMATIC AZOSULFIDES AND ENOLATES IN DMSO

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Abstract The outcome of the reaction between azosulfides **1** and ketone enolates is influenced by the presence of suitable alkyl substituents on the aryl moiety of **1**. The system can thus be conveniently exploited for the selective synthesis of different classes of derivatives of remarkable applicative interest, namely α -aryl ketones, α -arylhydrazone ketones, or indazoles.

Along the line of our continuing interest in the behaviour of azosulfides **1** as effective $S_{RN}1$ arylating agents at carbon,¹ we have recently observed² that in the reaction of some arylazo *tert*-butyl sulfides (**1**: Ar = 2- or 4- $R^4CH_2C_6H_4$, $R^1 = Bu^t$) with the strongly basic acetone enolate (**2**: $R^2 = H$, $R^3 = Me$) the expected arylation to **3** competes with processes originating from the deprotonation of activated alkyl groups in Ar: thus arylhydrazones **4** or indazoles **5** are the main products in the presence of methylene groups *para* or *ortho* to the azothio function respectively (Scheme 1).

We herein report that the phenylazo and the *para*-tolylazo *tert*-butyl sulfides

Scheme 1

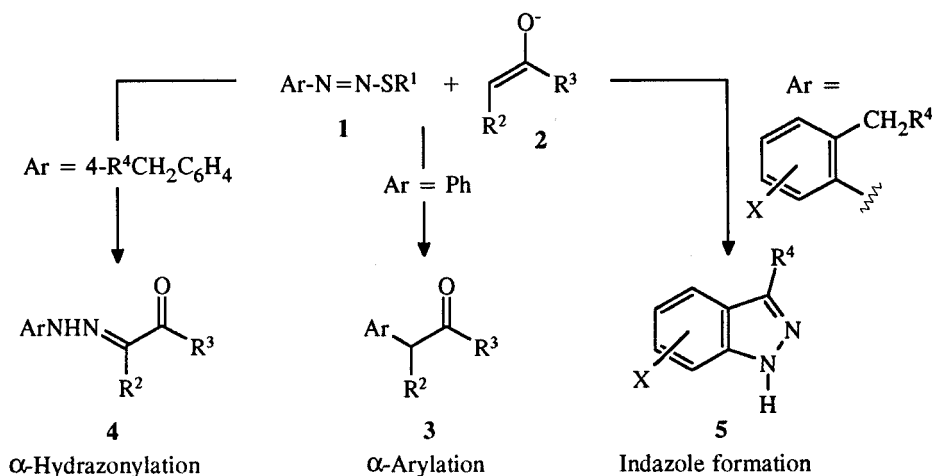


Table 1. Yields of selected 3-5 from azosulfides 1 (Scheme 1).

α -Arylketones 3 ^a Ar = Ph R ¹ = Bu ^t , R ² = H		α -Arylhydrazones 4 ^a Ar = 4-Tolyl R ¹ = Bu ^t , R ² = H		Indazoles 5				
Yield	R ³	Yield		R ¹	R ⁴	X	b	Yield
95%	Ph	71%		Bu ^t	H	H	A	84%
58%	2-MeOC ₆ H ₄	90%		"	Me	"	"	74%
77%	4-MeOC ₆ H ₄	92%		"	CH=CH ₂	"	"	93%
48%	3-thienyl	89%		"	H	5-MeO	"	73%
				Ph	"	6-NO ₂	B	100%

^aReactions carried out at room temp. with 10 mol. equiv. of enolate in DMSO. ^bConditions: A = Bu^tOK (10 mol. equiv.)/DMSO, r.t.; B = DBU (10 mol. equiv.)/MeCN, r.t.

have been found to selectively behave as effective α -aryllating or α -arylhyaazonylating agents respectively of aryl methyl ketones (Table 1). It is relevant to note that on one side the α -aryllation of alkyl aryl ketones is rather demanding when *e.g.* haloarenes are employed in similar S_{RN}1 processes.³ The interest in new and versatile synthetic approaches to arylhydrazones is in turn justified by their manifold exploitation, *e.g.* as precursors of aminoderivatives.⁴

As a concomitant project, the indazole synthesis has been optimized by replacing the enolate with a more suitable base and successfully applied to a number of *ortho*-alkylated azosulfides, leading to derivatives substituted either in the benzene ring or at C-3 (Table 1).

Studies are in progress in order to better define scope and limitations of the described processes.

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