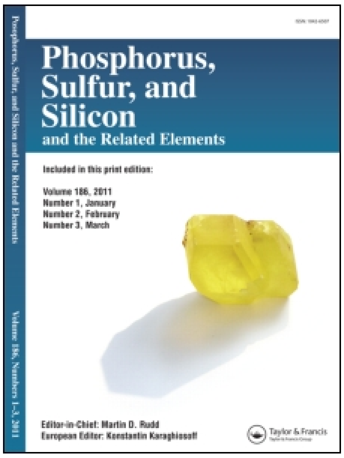

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Competitive Pathways in the Reaction between Aromatic Azosulfides and Enolates in DMSO

Carlo Dell'erba[a]; Marino Novi[a]; Giovanni Petrillo[a]; Cinzia Tavani[a]
[a] Istituto di Chimica Organica dell'Università and C.N.R. Centro di Studio sui Diariloidi e loro Applicazioni, Genova, Italy

To cite this Article Dell'erba, Carlo , Novi, Marino , Petrillo, Giovanni and Tavani, Cinzia(1993) 'Competitive Pathways in the Reaction between Aromatic Azosulfides and Enolates in DMSO', Phosphorus, Sulfur, and Silicon and the Related Elements, 74: 1, 409 — 410

To link to this Article: DOI: 10.1080/10426509308038139

URL: http://dx.doi.org/10.1080/10426509308038139

Phosphorus, Sulfur, and Silicon, 1993, Vol. 74, pp. 409–410
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

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

CARLO DELL'ERBA, MARINO NOVI, GIOVANNI PETRILLO, and CINZIA TAVANI
Istituto di Chimica Organica dell'Università and C.N.R. Centro di Studio sui Diariloidi e loro Applicazioni, Corso Europa 26, Genova, I-16132, Italy.

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-arylhydrazono 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 observed[2] 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

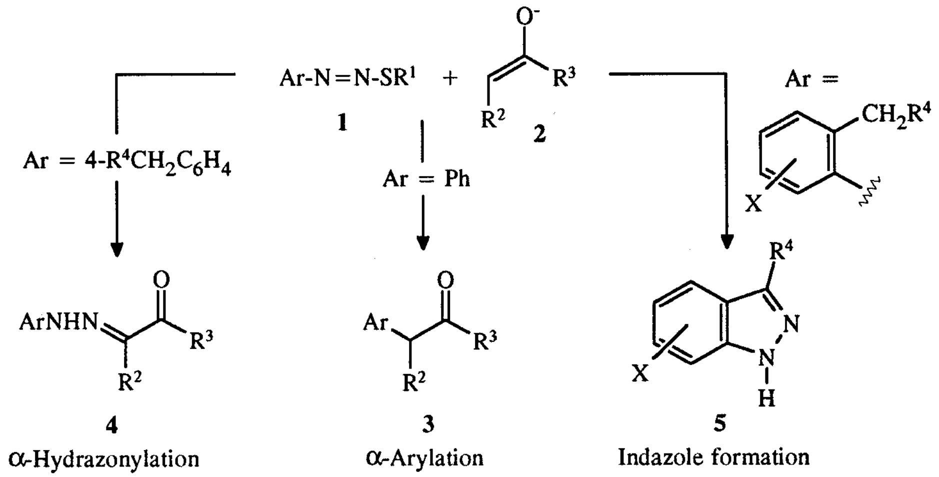

Table 1. Yields of selected **3**-**5** from azosulfides **1** (Scheme 1).

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-$MeOC_6H_4$	90%	"	Me	"	"	74%
77%	4-$MeOC_6H_4$	92%	"	$CH=CH_2$	"	"	93%
48%	3-thienyl	89%	"	H	5-MeO	"	73%
			Ph	"	6-NO_2	B	100%

^{a}Reactions carried out at room temp. with 10 mol. equiv. of enolate in DMSO. ^{b}Conditions: 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-arylating or α-arylhydrazonylating agents respectively of aryl methyl ketones (Table 1). It is relevant to note that on one side the α-arylation 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.

AKNOWLEDGMENT. Financial support from MURST is gratefully aknowledged.

REFERENCES

1. C. Dell'Erba, M. Novi, G. Petrillo, C. Tavani, and P. Bellandi, Tetrahedron, 47, 333 (1991), and references therein; G. Petrillo, M. Novi, C. Dell'Erba, C. Tavani, and G. Berta, Tetrahedron, 46, 7977 (1990); G. Petrillo, M. Novi, C. Dell'Erba, and C. Tavani, Tetrahedron, 47, 9297 (1991).
2. C. Dell'Erba, M. Novi, G. Petrillo, and C. Tavani, Tetrahedron, 48, 325 (1992).
3. R. K. Norris, in Comprehensive Organic Synthesis, edited by M. F. Semmelhack (Pergamon Press, New York, 1991), Vol. 4, pp. 451-482.
4. T. Sakakura and M. Tanaka J. Chem. Soc., Chem. Commun., 1309 (1985); T. Sakakura, M. Hara, and M. Tanaka, J. Chem. Soc., Chem. Commun., 1545 (1985).