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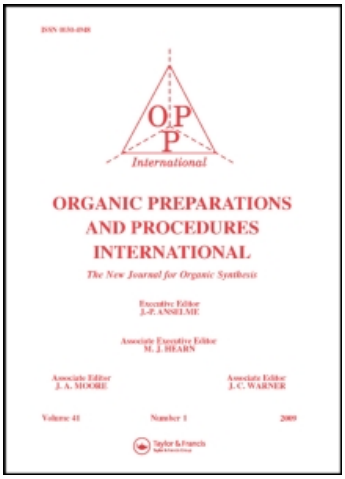

Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

A CONVENIENT PREPARATION OF 4-ARYL-1,2,4-TRIAZOLINE-3,5-DIONES

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To cite this Article Wamhoff, Heinrich and Wald, Klemens(1975) 'A CONVENIENT PREPARATION OF 4-ARYL-1,2,4-TRIAZOLINE-3,5-DIONES', Organic Preparations and Procedures International, 7: 5, 251 — 253
To link to this Article: DOI: 10.1080/00304947509355156
URL: http://dx.doi.org/10.1080/00304947509355156

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ORGANIC PREPARATIONS AND PROCEDURES INT. 7(5), 251-253 (1975)

A CONVENIENT PREPARATION OF 4-ARYL-1,2,4-TRIAZOLINE-3,5-DIONES

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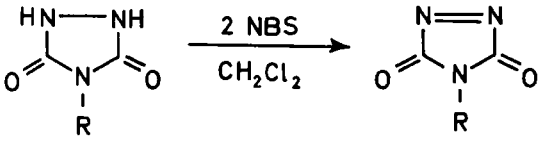
A recently published [1] new synthesis of 4-phenyl-1,2,4-triazoline-3,5-dione (IIa) prompts us to report an alternative preparation of IIa and related compounds. As part of our continuing investigations on these compounds, we have found that the oxidation of 1,2-disubstituted hydrazines with N-bromosuccinimide described by Bock and co-workers some time ago,[2] offers a facile method for the transformation of 4-aryl- and 4-benzyl-urazoles (Ia-d) into the corresponding 1,2,4-triazoline-3,5-diones (IIa-d). For example, analytically pure IIa is obtained in 78% yield by oxidation of 4-phenyl-urazole Ia.[3]



Ia-d IIa-d

I,II	R
a	C_6H_5-
b	4-ClC_6H_4-
c	3,4-$Cl_2C_6H_3$-
d	$C_6H_5CH_2$-

However, this method failed with compounds, such as 4-t-butyl- or 4-p-nitrophenyl-1,2,4-triazoline-3,5-diones, because hydrolysis of the N-substituents during removal of

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the accompanying succinimide with water.

Earlier procedures employed t-butylhypochlorite [3] or dinitrogen tetroxide [4] as the oxidizing agents with comparably high yields. The major improvement offered by NBS is the easy and simple handling. In trichloroacetyl isocyanate/DMSO,[1] a 98% yield of triazoline in solution is reported, but on isolation the yield decreases to 20%.

Photochemical and thermal reactions of IIa-d are reported elsewhere.[5]

Table 1.-Analytical and UV Data of 1,2,4-Triazoline-3,5-dione

II	Yield [%]	mp [a] [°C]	UV, λ_{max} [nm] (ε) [c]	Analysis calcd. (found) C	H
a	78	166-172	532 (147) [e]	(lit.[3] mp. 165-175°)	
b	73	130-132	528 (98)	45.82	1.91
				(45.85)	(2.14)
c	75	113-115	527 (45)	d	
d	84	66	548 (119), 527 (154)	57.11	3.70
				(57.44)	(3.67)

a) In most cases decomposition at lower temperature ranges. b) Decomposition range. c) In acetonitrile. d) A satisfactory elemental analysis could not be obtained due to the instability of IIc. e) Lit.[1] 525 (157) acetonitrile; lit.[3] 532 (171) dioxane; lit.[4] 545 (135) methylene chloride.

EXPERIMENTAL [6]

General Procedure for Preparation of IIa-d. - To an ice-cooled suspension of the urazoles Ia-d (20 mmoles) in methylene

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chloride (200 ml) was added N-bromosuccinimide (7.12 g; 40 mmoles) and the mixture was stirred for an additional 15 min. The red solution was extracted three times with water, dried (magnesium sulfate) and evaporated carefully (bath temp. < 35°C). The resultant crude products are almost of analytical purity and ready for subsequent reactions. Further purification may be achieved by sublimation (90-100° at 0.1 Torr). IIc could not be sublimed.

Acknowledgement. - This work was supported by grants from the Deutsche Forschungsgemeinschaft and from the Fonds der Chemischen Industrie. Gifts of isocyanates from BAYER AG are gratefully acknowledged.

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(Received October 10, 1975)