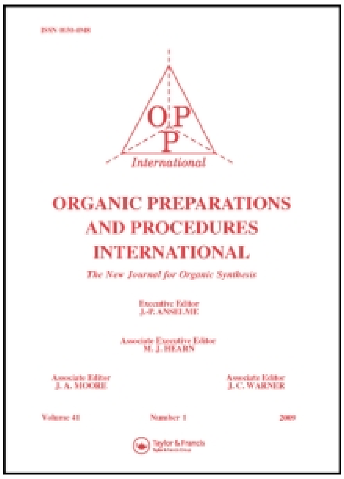

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AN EFFICIENT OXIDATION ARYLSEMICARBAZIDES TO THE AZO UREAS

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AN EFFICIENT OXIDATION ARYLSEMICARBAZIDES TO THE AZO UREAS

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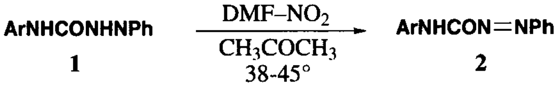
Nitrogen oxides have been used to convert ketals into ketones,[1] to oxidize benzyl alcohols into benzaldehydes,[2] and ethers and alcohols to the corresponding aldehydes and ketones.[3-5] However, the oxidation of the NHNH bond using nitrogen dioxide has not been reported. We now describe an efficient oxidation of aryl semicarbazides to 1,4-disubstituted azo ureas using nitrogen dioxide absorbed in N,N-dimethylformamide (DMF). While most oxidizations with nitrogen dioxide involve NO_2 catalyzed by silica gel,[1,4] the use of DMF to absorb NO_2 and of DMF-NO_2 as an oxidizing system has not been reported previously.

Azo compounds are widely utilized as dyes and analytical reagents. They can also be used as materials for non-linear optics and for storage optical information in laser dish.[6] Recently, many noteworthy studies have shown that azobenzene derivatives possess excellent optical memory and photoelectric properties.[7] The preparation of ordinary azo compounds has been described in many references.[8,9] However, those compounds generally bear alkyl or aryl groups on both sides of the azo linkage (-N=N-). In this paper, eight new azo ureas in which one side of the azo group is connected to a carbonyl group have been synthesized in good yield under mild conditions.



$$\underset{\mathbf{1}}{\text{ArNHCONHNPh}} \xrightarrow[\substack{CH_3COCH_3 \\ 38\text{-}45^\circ}]{DMF\text{-}NO_2} \underset{\mathbf{2}}{\text{ArNHCON=NPh}}$$

a) Ar = p-FC_6H_4 b) Ar = o-ClC_6H_4 c) Ar = m-ClC_6H_4 d) Ar = p-ClC_6H_4
e) Ar = o-BrC_6H_4 f) Ar = m-BrC_6H_4 g) Ar = p-BrC_6H_4 h) Ar = p-IC_6H_4

In order to optimize reaction conditions, the effects of the reaction temperature and mole ratio of starting materials were studied. These experiments showed that it was best that the temperature was within 38-45°. Below 35°, the oxidation of starting material was very slow and almost no product was obtained. Above 50°, the yield decreased because of NO_2 being desorbed from DMF and not being consumed efficiently. The best mole ratio of aryl substituted semicarbazide and DMF-NO_2 was 1:1.3. With the use of a large excess of DMF-NO_2, no over oxidation product was obtained, showing DMF-NO_2 to be a mild oxidant.

EXPERIMENTAL SECTION

Melting points were determined with a Kofler micro melting point apparatus and are uncorrected. IR spectra were recorded on a SP3-300 spectrophotometer in KBr. ^1H NMR spectra were measured on a JEOL-Fx-90Q spectrometer using TMS as internal standard and $CDCl_3$ as solvent. MS spectra were taken on a KRATOS-AEI-MS50 (U.K) spectrometer. Elemental Analyses were performed on a

Carlo-Erba 1102 elemental analyzer. 1,4-Disubstituted arylsemicarbazides (**1a-1h**) were prepared by the literature methods.[10,11]

Preparation of DMF-NO_2.- In a glass-ring packed tower [900mm x 20mm(i.d.)], the absorption was performed by spraying DMF from the top of tower with a sprayer while introducing NO_2 from the bottom of tower. The absorption efficiency of NO_2, which was determined by Saltzman's Reagent,[12] was found to reach to 97% at 200mL/min gas flow rate. The concentration of NO_2 in DMF was 6.1mmol/g, and this was determined by reacting DMF-NO_2 with excess aqueous sodium hydroxide and then titrating the remains with hydrochloric acid.[13] DMF-NO_2, a dark-green liquid, is a stable, mild and efficient oxidizing agent, which showed no obvious dangerous properties.[14]

TABLE 1. Yields, mps, Color and Elemental Analyses of Compounds **2**

Cmpd	Time (min)	Yield (%)	mp. (°C)	Color	Elemental Analyses (Found) C	H	N
2a	25	91	106-107	yellow	64.19 (64.02)	4.14 (4.39)	17.28 (17.44)
2b	20	89	83-84	orange-red	60.13 (60.29)	3.88 (3.73)	16.18 (15.96)
2c	20	94	87-88	red	60.13 (60.34)	3.88 (3.96)	16.18 (16.35)
2d	20	92	141-142	red	60.13 (59.97)	3.88 (3.68)	16.18 (16.03)
2e	25	91	72-73	red	51.49 (51.38)	3.33 (3.14)	13.86 (13.69)
2f	20	96	94-95	orange	51.49 (51.68)	3.33 (3.50)	13.86 (13.97)
2g	20	99	148-149	red	51.49 (51.24)	3.33 (3.57)	13.86 (13.84)
2h	30	90	134-135	orange-red	44.47 (44.36)	2.87 (2.68)	11.97 (11.79)

TABLE 2. IR , 1H NMR and MS Spectra of Compounds **2**

Cmpd	IR(cm^{-1}) N-H	C=O	N=N	^1H NMR (δ, ppm) ArH	NH	MS (m/z, %)
2a	3340	1710	1425	7.09-8.04 (m, 9H)	8.44 (s, 1H)	243 (M^+, 143) 110 (100)
2b	3335	1700	1425	7.16-8.62 (m, 9H)	8.56 (s, 1H)	259 (M^+, 9.6) 126 (100)
2c	3260	1685	1430	7.12-8.20 (m, 9H)	8.58 (s, 1H)	259 (M^+, 11.7) 126 (100)
2d	3325	1680	1440	7.20-8.06 (m, 9H)	8.60 (s, 1H)	259 (M^+, 18.7) 126 (100)
2e	3280	1685	1440	7.14-8.60 (m, 9H)	8.56 (s, 1H)	304 (M^+, 8.4) 171 (100)
2f	3320	1700	1435	7.10-8.10 (m, 9H)	8.57 (s, 1H)	304 (M^+, 10.2) 171(100)
2g	3325	1680	1450	7.25-8.00 (m, 9H)	8.56 (s, 1H)	304 (M^+, 11.1) 171 (100)
2h	3300	1680	1440	7.25-7.98 (m, 9H)	8.57 (s, 1H)	351 (M^+, 6.2) 218 (100)

General Procedure.- A solution of **1a-1h** (2mmol) in acetone(20-30mL) was stirred at 40° and DMF-NO_2 (0.43g, 2.6mmol) was added dropwise. The mixture was stirred at about 40°. After 20-30 minutes, the color of solution changed from yellow to orange then orange-red. Cold water (50mL) was added slowly. The corn yellow, orange or orange-red flocculent precipitate was collected, washed with water and dried under vacuum. The products (**2a-2h**) were obtained in excellent yield (89-99%).

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14. When heated above 80°, a small amount of NO_2 is desorbed from DMF; it may be absorbed into aqueous sodium hydroxide.

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