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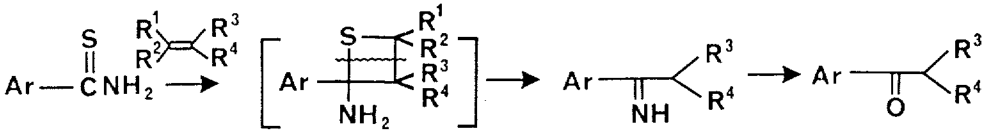
PHOTOREACTION OF ARENECARBOTHIOAMIDES WITH FURANS.[1] THE REGIOSELECTIVE PHOTOINDUCED ACYLATION AT THE 3-POSITION OF FURANS

Kazuaki Oda* and Minoru Machida
Faculty of Pharmaceutical Sciences, Higashi-Nippon-Gakuen University,
Ishikari-Tobetsu, Hokkaido 061-02, Japan
Yuichi Kanaoka
Faculty of Pharmaceutical Sciences, Hokkaido University, Sapporo 060, Japan

Abstract: Irradiation of arenecarbothioamides (1,4) with furan (2) gave regioselectively 3-aroylfurans (3,5).

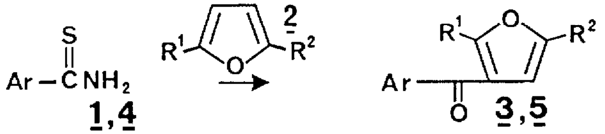
The most useful method for the preparation of aryl ketones is probably the Friedel-Crafts acylation, by which many heterocyclic systems such as furans and thiophenes may be acylated in good yields. For example, an acyl group is introduced regioselectively at the 2-position of an unsubstituted furan. During the course of our systematic studies on photochemistry of thioamide and thioimide systems, we found that benzthioamide undergoes Paterno-Büchi type reaction with olefins to give thietane followed by photochemical fission leading to acyl compounds (Chart I).[2] These findings led us to develop the application of this photoinduced acylation of furans and other cyclic olefins.

Chart I



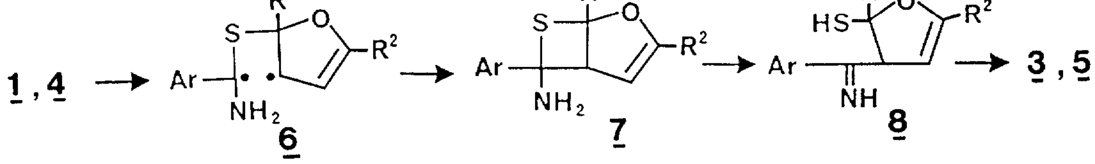
Photoreactions of arenecarbothioamides (1,4) with furan derivatives (2) were carried out in benzene using a high pressure mercury lamp through a Pyrex filter under nitrogen atmosphere. The results are listed in Table I.[3] Irradiation of benzenecarbothioamide (1) and twenty equivalents of furan (2a) for 2h gave exclusively 3-benzoylfuran (3a) in 72% yield. Similary in the presence of 2-methylfuran (2b) and 2,5-dimethylfuran (2c), 4-benzoyl-2-methylfuran (3b) and 3-benzoyl-2,5-dimethylfuran (3c) were obtained in 45% and 48% yield, respectively. Probably 3-benzoylfuran (3) arises from the initially formed thietanes followed by subsequent photochemical fission of the thietane ring, and then by hydrolysis of generated imines (8) during its workup such as chromatography (Chart II). Thus, by use of a excess of furans, 1 underwent efficiently the Paterno-Büchi type reaction leading ultimately to 3-benzoylfuran (3). In order to see the generality of this reaction, photoreactions of heteroaromatic carbothioamides (4) were performed under similar conditions. As expected, 3-aroylfurans (5) were obtained in moderate yields. Further, in the case of thiophene, benzenecarbothioamide (1) gave 3-benzoylthiophene (mp. 63-64°C,

Table I



	Arenecarbothioamide		Furan	Time(h)		3-Aroylfuran mp(°C)	Yield(%)
1	Ar=benzene	2a	$R^1=R^2=H$	2	3a	oil	72
		2b	$R^1=H$, $R^2=CH_3$	10	3b	oil	45
		2c	$R^1=R^2=CH_3$	10	3c	oil	48
4a	Ar=3-pyridine	2a		10	5a	110-111	38
4b	=4-pyridine	2a		10	5b	79.5-80	31
4c	=2-thiophene	2a		10	5c	56-57(57)[4]	44
4d	=2-furan	2a		10	5d	46-47(46)[4]	39

Chart II



lit.[5] mp. 64.5°C) in 47% yield.

Furans undergo electrophilic substitution, with exceptional ease, at the 2-position.[6] In literature only one example of 3-acylation has been recorded and that was observed on photoaddition of 1,3,4-oxadiazoles to furan.[5] The photoreaction of arenecarbothioamides (1,4) described in the present communication will provide a practical synthetic route to 3-acyl derivatives of π-excessive heteroaromatics and other cyclic unsaturated systems, otherwise inaccessible by conventional thermal substitutions.

References and Notes

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