銅触媒による 2,2'-ジチオジアニリン類を用いたベンゾチアゾール誘導体の合成

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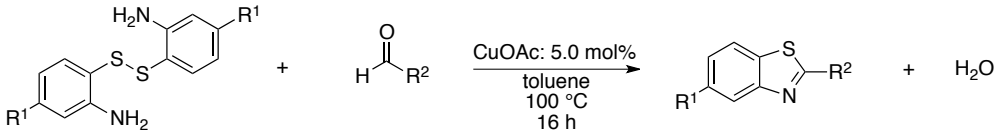
Preparation of Benzothiazole Derivatives from 2,2'-Dithiodianilines under Copper Catalyst (*Graduate School of Science and Engineering, Yamagata University*) ○Keisuke Minami, Maki Minakawa

The synthesis of benzothiazole derivatives is important because of their diverse biological, pharmaceutical applications and interesting chemical properties. Here, we report that Cu-catalyzed reaction of 2,2'-dithiodianilines with aldehydes for the preparation of benzothiazole derivatives. Thus, the reaction of 2,2'-dithiodianiline (**1a**: 0.1 mmol) with ethyl glyoxylate (**2a**: 47% in toluene, 0.3 mmol) in the presence of copper acetate (I) (5.0 mol% on the base on 2,2'-dithiodianiline) at 100 °C for 16 h afforded benzothiazole **3aa** in 99% yield (Scheme 1). Under similar reaction conditions, the reaction of dithiodianilines **1a**–**b** with aldehydes **2a**–**g** also proceeded to form the corresponding benzothiazole derivatives (58–95% yield, 11 examples).
Keywords : Copper Acetate(I); Benzothiazole; 2,2'-Dithiodianiline; S-S bond cleavage

ベンゾチアゾール誘導体の合成は，その多様な生物的, 製薬的用途，および興味深い化学的性質のため重要である．本研究では, 銅触媒を用いたジチオジアニリン類とアルデヒド類によるベンゾチアゾール誘導体の合成について検討した. 即ち, 2,2'-ジチオジアニリン(**1a**: 0.1 mmol)とグリオキシル酸エチル(**2a**: 0.3 mmol)は，酢酸銅(I)(5.0 mol% on the base on 2,2'-dithiodianiline)存在下, 100 °C, 16 時間の反応条件でベンゾチアゾール誘導体 **3aa** を収率 99%で与えた (Scheme 1). 同様の触媒反応条件下, ジチオジアニリン **1a**–**b** とアルデヒド類 **2a**–**g** を用いた場合にも反応は進行し, 対応するベンゾチアゾール誘導体を得た(58–95% yield, 11 examples).



1a–b **2a–g** **3**

1a: R^1 = H
1b: R^1 = Cl

2a: R^2 = COOEt
2b: R^2 = C_6H_5
2c: R^2 = 4-$OMeC_6H_4$
2d: R^2 = 4-MeC_6H_4
2e: R^2 = 4-FC_6H_4
2f: R^2 = 4-ClC_6H_4
2g: R^2 = 4-$CF_3C_6H_4$

3aa: R^1 = H, R^2 = COOEt : 99% yield
3ab: R^1 = H, R^2 = C_6H_5 : 84% yield
3ac: R^1 = H, R^2 = 4-$OMeC_6H_4$: 69% yield
3ad: R^1 = H, R^2 = 4-MeC_6H_4 : 68% yield
3ae: R^1 = H, R^2 = 4-FC_6H_4 : 95% yield
3af: R^1 = H, R^2 = 4-ClC_6H_4 : 83% yield
3ag: R^1 = H, R^2 = 4-$CF_3C_6H_4$: 94% yield

3ba: R^1 = Cl, R^2 = COOEt : 79% yield
3bb: R^1 = Cl, R^2 = C_6H_5 : 71% yield
3bc: R^1 = Cl, R^2 = 4-$OMeC_6H_4$: 58% yield
3bg: R^1 = Cl, R^2 = 4-$CF_3C_6H_4$: 88% yield

Scheme 1. Reaction of Dithiodianilines with Aldehydes Under CuOAc Catalyst

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