

PREPARATION AND THERMAL PROPERTIES OF 2-ARYL-5-BENZOYLTHIO-
1,3,4-OXADIAZOLES

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Abstract — Novel type of thioesters, 2-aryl-5-benzoylthio-1,3,4-oxadiazoles ($3a-3d$), were prepared by the elaborate benzoylation of 2-aryl-1,3,4-oxadiazoline-5-thiones ($1a-1d$), and their thermal behavior was elucidated by differential thermal analysis (DTA).

Recently, the transformation of carboxyl group to a reactive form has become of interest in polyamide syntheses under mild conditions.¹⁻³

In our preceding paper³, it has been described in detail that 2-aryl-4-benzoyl-1,3,4-oxadiazoline-5-thiones ($2a-2c$), obtained by the conventional benzoylation (0°C to room temperature) of $1a-1c$ ⁴, have showed enhanced reactivity to a nucleophilic attack. We have found that in kinetically controlled benzoylation (low temperatures) $1a-1d$ are attacked exclusively at the sulfur atom to afford $3a-3d$. Nothing has been reported to date on the synthesis of such type of oxadiazole derivatives, probably because oxadiazoles easily tautomerize to thermodynamically more stable oxadiazolines. Therefore, it is worthwhile to prepare S-benzoyl derivatives of oxadiazoles and to elucidate their thermal behavior.

This paper describes the successful synthesis of novel type of thioesters $3a-3d$ by the elaborate benzoylation of $1a-1d$ and their thermal properties.

The reaction conditions favorable for the formation of S-benzoyl thioesters were determined for the preparation of $3a$ from $1a$ with benzoyl chloride. The reaction

in tetrahydrofuran (THF) in the presence of triethylamine (TEA) yielded a mixture of two products, depending on the reaction temperature; the reaction above -10°C gave rise to only $2a$, whereas the product prepared -20 to -10°C contained a small amount of $3a$ in addition to $2a$ and its content increased with decreasing reaction temperature. Finally, $3a$ alone could be synthesized below -50°C .

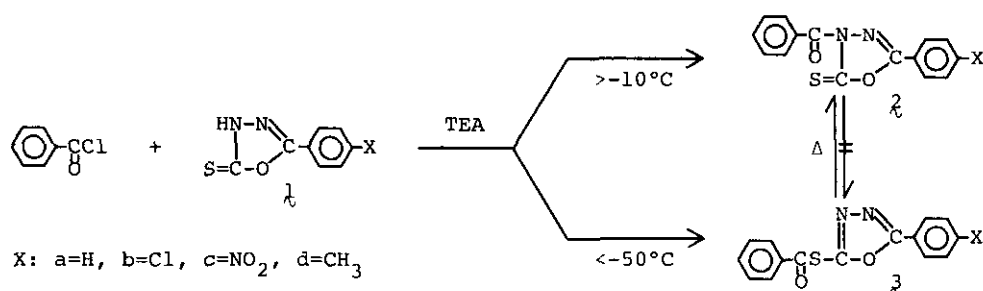


Table 1. Yield, thermal properties and elemental analyses of $2a$ - $3d$

Compound	Yield (%)	mp ^a (°C)	cp ^b (°C)	mp ^c (°C)	Found (Calcd)		
					C (%)	H (%)	N (%)
$2a$	98	106	121	135 ^d	63.92 (63.81)	3.53 3.57	9.94 9.93
$2b$	90	123	125	162 ^e	56.89 (56.87)	2.84 2.86	8.85 8.85
$2c$	96	115	119	209 ^f	53.62 (54.04)	2.67 2.77	12.58 12.84
$2d$	93	120	126	150	64.82 (64.85)	4.04 4.08	9.48 9.46

^a Melting temperature of 2 . ^b Crystallization temperature of 2 .

^c Melting temperature of 2 . ^d lit.³ mp 136-137°C. ^e lit.³ mp 159-160°C.

^f lit.³ mp 207-208°C.

Similarly, other thioesters were also prepared in high yields (Table 1). The general procedure was as follows: To a stirred and cooled (-75 to -50°C) solution of 1 (20 mmol) and TEA (24 mmol) in THF (300 ml) was added a solution of benzoyl chloride (20 mmol) in THF (50 ml) over a 15-min period. After stirring for 30 min at that temperature, the mixture was poured into ice water (1000 ml). The precipitate was filtered off, washed with ice water, and dried in vacuo.

The DTA curve for $3a$ exhibited three sharp peaks (Fig. 1): An endothermic peak caused by melting at 106°C , an exothermic peak due to the heat of crystallization of rearranged compound at 121°C , and a melting peak of rearranged compound at 135°C . The ir spectrum and melting peak of the substance obtained after thermal rearrangement were identical with those of authentic N-benzoyl derivative $2a$.³ After the specimen was heated to a temperature between the exothermic and second endothermic peaks (curve B) and then cooled to room temperature, peaks due to the first melting and the crystallization disappeared (curve C). Similar thermal behavior was also observed for other thioesters (Table 1). Therefore, this rearrangement is irreversible.

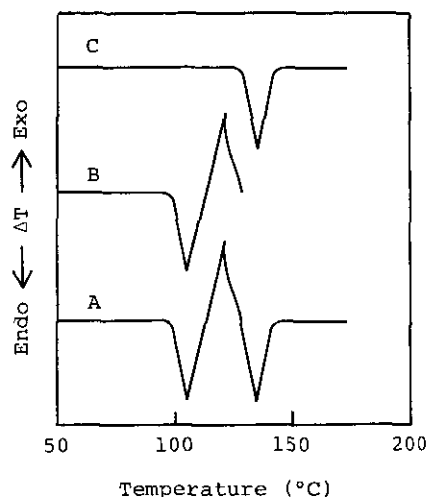


Fig. 1 DTA curves for $3a$ in air (5K/min).

In conclusion, a new type of thioesters $3a-3d$ alone could be prepared from the benzoylation of $1a-1d$ under kinetically controlled conditions ($<-50^{\circ}\text{C}$). These thioesters, however, irreversibly tautomerize even at relatively low temperature to thermodynamically more stable N-benzoyl derivatives $2a-2d$. Further investigation on their aminolyses and an expansion to polyamide synthesis under mild conditions are now in progress.

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