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THE REACTION OF 2,5,5-TRIPHENYL-2-OXAZOLIN-4-ONE WITH PHOSPHORUS PENTASULFIDE

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Abstract – 2,5,5-Triphenyl-2-oxazolin-4-one (3), when refluxed with phosphorus pentasulfide in xylene, is transformed into N-(3-phenyl-2-benzo[b]thienyl)-thiobenzamide (7).

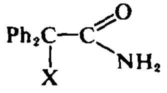
Zusammenfassung – Beim Kochen mit Phosphorpentasulfid in Xylol wird das 2,5,5-Triphenyl-2-oxazolinon-(4) (3) in N-(3-Phenyl-2-benzo[b]thienyl)-thiobenzamid (7) umgewandelt.

In the preceding paper[1] 2,5,5-triaryl-2-thiazolin-4-ones (*e.g.* **1**) were transformed in reaction with phosphorus pentasulfide into the corresponding N-(3-aryl-2-benzo[b]thienyl)-thiobenzamides (*e.g.* **7**). The analogous imidazole derivatives (*e.g.* **2**) furnish under comparable conditions the thiones (*e.g.* **5**) corresponding to the starting compounds.[2] The latter normal thiation reaction also occurs in triarylthiazolinones, the thiones (*e.g.* **4**) thus obtained are, however, unstable and are themselves transformed into the corresponding benzothienyl-thiobenzamides (*e.g.* **7**).[1]

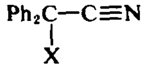
The reactivity of 2,5,5-triphenyl-2-oxazolin-4-one (**3**) towards phosphorus pentasulfide was therefore next studied.

The oxazolinone **3** has been prepared by reacting 4,4-diphenyl-Δ^2-1,2,3-triazolin-5-one (**9**) with benzoyl chloride[3] or by treatment of the halogenoimide **10** with sodium hydride;[4] owing to the potential tautomerism and ambident reactivity of **9**, however, the first synthesis is not structure proving.

We have prepared compound **3** by reacting benzilamide (**11**) with benzoyl chloride and ring closure of the resulting N-benzoyl derivative **12**. When **11** was treated with excess benzoyl chloride, the cyano derivative **13** was obtained which results also from α-bromo-α,α-diphenylacetonitrile (**14**) with silver benzoate.[3]



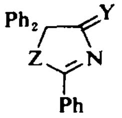
11: X = OH
12: X = OBz



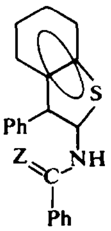
$$\begin{array}{l}Ph_2C{-}C{\equiv}N\\ \quad\ \ |\\ \quad\ \ X\end{array}$$

13: X = OBz
14: X = Br

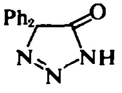
When **3** was treated with phosphorus pentasulfide in boiling xylene, compound **7**[1] resulted. It seems plausible to assume that at least two intermediates, **6** and **8**,[1] are involved in the latter transformation. The reaction was, therefore, followed by TLC, but the presence of **8** in the mixture could not be definitely established. Small amounts of an unstable red substance (which could not be isolated in pure crystalline form) were, however, detected in the mixture; since the corresponding thiazolinethiones (*e.g.* **4**) are also



1: Z = S; Y = O
2: Z = N—Me; Y = O
3: Z = O; Y = O
4: Z = S; Y = S
5: Z = N—Me; Y = S
6: Z = O; Y = S



7: Z = S
8: Z = O



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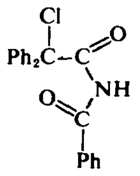

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red,[1] the above substance may well be identical with the compound sought (6). The reason why only traces of compound **8** are present in the thiation mixture seems to be that **8** is rapidly transformed into **7** under the reaction conditions applied.[1]

We attempted to obtain the oxazolinethione **6** by an alternative independent route, the first step of which consisted in the addition of hydrogen sulfide to the nitrile group of **13**. However, on hydrogen sulfide treatment of **13** the benzoyloxy group was eliminated and α,α-diphenylthioacetamide was obtained.

EXPERIMENTAL

2,5,5-*Triphenyl*-2-*oxazolin*-4-*one* 3

Benzoyl chloride (4·8 ml; 42 mmoles) was added under continuous stirring and cooling to an anhyd pyridine soln (40 ml) of **11** (9·0 g; 40 mmoles) at such a rate that the temp did not exceed 10°. The mixture was allowed to stand overnight (pyridinium chloride separated in crystalline form) and subsequently poured into about 5 times its volume of water. The yellow oily product obtained was taken up in chloroform; the aqueous layer was extracted with the same solvent and the combined chloroform solns were washed with 10% HCl, water, 5% $NaHCO_3$ aq and water and dried over $MgSO_4$.

Difficulties were experienced during attempted crystallization and purification of the yellow oil obtained on evaporation of the solvent, and the crude **12** was therefore refluxed for 1 hr with Ac_2O (100 ml) to yield, after evaporation of the solvent *in vacuo* and recrystallization of the residue from EtOH (30 ml), 3·0 g (24%) of **3**, colourless crystals, m.p. 168–170°, lit.[3] 169°; UV(EtOH): 202 (4·72), 267 (4·35); IR(KBr): $\nu_{C=O}$ 1750, $\nu_{C=N}$ 1550.

α-*Cyanobenzhydryl benzoate* (13)

Benzoyl chloride (7·3 ml; 66 mmoles) was added to an anhyd pyridine soln (20 ml) of **11**. The resulting mixture was allowed to stand overnight (crystalline pyridinium chloride was deposited) and poured into about 4 times its volume of water. A red oil separated and slowly turned crystalline. The product was thoroughly washed with water and recrystallized from EtOH (charcoal) to yield 4·8 g (78%) of **13**, m.p. and mixed m.p. with an authentic sample prepared according to l.c.[3] 135–137°, lit.[3] 138·5°; UV(EtOH): 227 (4·25); 260 (3·20), sh; IR-(KBr): ester bands 1740, 1260, 1070.

Reaction of 2,5,5-*triphenyl*-2-*oxazolin*-5-*one* (3) *with phosphorus pentasulfide*

(a) A mixture of **3** (1·5 g; 5 mmoles), P_2S_5 (1·1 g; 5 mmoles) and anhyd xylene (15 ml) was refluxed for 4 hr. Light petroleum (50 ml) was added to the soln after being allowed to cool. The yellow crystals of crude **7** separated and were isolated and purified as described earlier[1] to yield 0·5 g (30%) of pure **7**, m.p. 191–193°, identical in all respects (m.p., mixed m.p., IR spectra, TLC) with an authentic sample.[1]

(b) When the reaction was performed in dioxane **7** was obtained in less pure form and lower yields.

(c) A mixture of **3** (1·5 g; 5 mmoles), P_2S_5 (1·1 g; 5 mmoles) and THF (15 ml) was refluxed under continuous stirring for 20 hr. The insoluble material was filtered off, the filtrate was diluted with water and extracted with chloroform. The chloroform soln was washed with $NaHCO_3$aq and examined by TLC (adsorbent: Kieselgel G; development: benzene; reference substances: **3**, **7** and **8**; detection: iodine vapour). Besides **7**, considerable amounts of P_2S_5 as well as of the starting substance **3**, and a red compound with the highest R_f value among the compounds present (**6**?), a very faint spot with an R_f value identical with that of compound **8** could only be detected.

α,α-*Diphenylthioacetamide*

The benzoate **13** (7·8 g; 25 mmoles) was dissolved in a mixture of dry pyridine (15 ml) and dry triethyl amine (3·5 ml). A stream of H_2S was introduced for 8 hr into the soln which became black and, subsequently, was allowed to stand overnight. The introduction of H_2S was then continued for another 2 hr. Subsequently the soln was diluted with water to about 150 ml. A red oil, which turned crystalline on rubbing, was deposited. The product was washed with water; when recrystallised from a large amount of EtOH, 0·5 g of S was obtained. The filtrate of the latter was again evaporated to dryness and the resulting brown oil recrystallised from 150 ml CCl_4 to yield 2·7 g (32%) of **13**, colourless crystals, m.p. 147–151°, lit.[5] 153–154°, identical according to IR spectra with an authentic sample prepared according to the general method[6] for the preparation of thioamides.

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