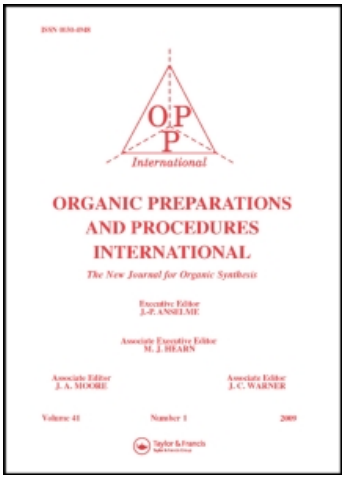


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

THE THERMAL CYCLYZATION OF DIETHYL METHANETRICARBOXYLATE THIOANILIDE

H. Junek[a]; A. Metallidis[a]; E. Ziegler[a]
[a] Institut für Organische Chemie Universitat, Graz, Austria

To cite this Article Junek, H. , Metallidis, A. and Ziegler, E.(1970) 'THE THERMAL CYCLYZATION OF DIETHYL METHANETRICARBOXYLATE THIOANILIDE', Organic Preparations and Procedures International, 2: 3, 161 — 165
To link to this Article: DOI: 10.1080/00304947009458650
URL: http://dx.doi.org/10.1080/00304947009458650

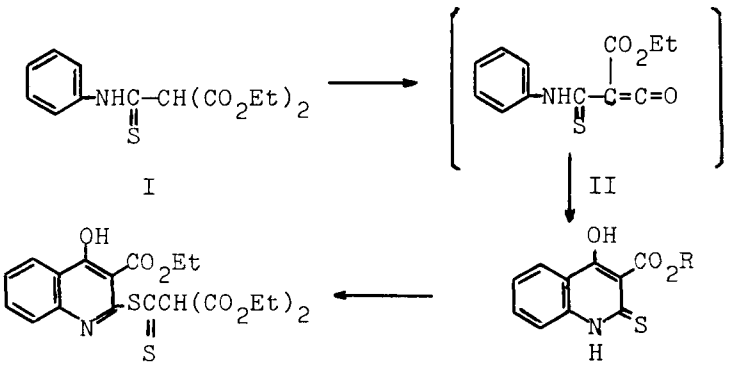
ORGANIC PREPARATIONS AND PROCEDURES 2(3), 161-165 (1970)

THE THERMAL CYCLYZATION OF DIETHYL METHANETRICARBOXYLATE THIOANILIDE

H. Junek, A. Metallidis and E. Ziegler
Institut für Organische Chemie
Universität Graz, Austria

The thermolysis of the diethyl methanetricarboxylate anilide gives good yields[1] of 2,4-dioxo-3,3-bis-(carboxanilino)-1,2,3,4-tetrahydroquinoline. Other derivatives of methanetricarboxylic acid[2] show similar properties. The present paper deals with the thermal behavior of the diethyl methanetricarboxylate thioanilide(I) under reduced pressure. Compound I was prepared from phenylisothiocyanate and diethyl sodio malonate.[3]

Partial decomposition of I into phenylisothiocyanate and



malonic ester can be demonstrated by gas chromatography when I is heated for 20 min. to 190°/10 mm. Hg.[4] However, two products can be isolated from the residue: ethyl 4-hydroxy-2-thiono-1,2-dihydroquinoline-3-carboxylate(III, 77%) and ethyl 4-hydroxy-2-(3,3-dicarbethoxy-2-thiono-1-thiapropyl)-quinoline-3-carboxylate(IV). The structure of the main product III was deduced from its hydrolysis to 4-hydroxy-2-dihydro-quinoline-3-carboxylic acid(V) and by its infrared spectrum. It exhibited associated OH and NH bands between 3280-2950 cm^{-1}, an ester C=O at 1690 cm^{-1}, while the C=C appeared at 1640 cm^{-1}. The aromatic peaks occur at 1610 and 1590 cm^{-1}, the thiurono peak at 1540 and the C=S at 1320 cm^{-1}. Compound IV is formed in small amount. Elemental analysis and molecular weight determination corresponds to the formula $C_{20}H_{21}NO_7S_2$. The infrared spectrum is quite similar to that of III, exhibiting an associated OH at 3000 cm^{-1}, a carbethoxy group at 1730 and 1690 cm^{-1}, aromatic bands at 1660 and 1600 cm^{-1}.

Previous investigations of the thermal decomposition of other methanetricarboxylate derivatives[1,2] suggest that I loses ethanol to form the ketene II primarily.[5] Stabilization of II by ring closure then leads to the quinoline III. On the other hand if aniline is eliminated from I, a thiodicarbethoxyketene should be obtained which then reacts with III to give IV. The thermolysis of the dianilide of methanetricarboxylic acid thioanilide(VI), methanetricarboxylic acid thioanilide nitrile[6] and the ethyl ester of acetylmalonic acid thioanilide[7] results only in decomposition; no cyclization products could be isolated.

EXPERIMENTAL

Preparation of III and IV. Diethyl methanetricarboxylate thioanilide(I, 5 g., 11 mmoles) is heated at 190°/10 mm. for 20 min. and the liquid reaction products removed by distillation. The residue is washed with ether and 1.7 g. (77%) of III is obtained. Recrystallization from dioxane yielded yellow needles, mp. 291°.

Calcd. for $C_{12}H_{11}NO_3S$: C, 57.82; H, 4.45; N, 5.61; S, 12.86.
Found: C, 57.75; H, 4.63; N, 5.58; S, 12.61.

Evaporation of the ethereal filtrate from the isolation of III gave IV (0.2 g.) which is washed with petroleum ether and recrystallized from ethanol to give yellow crystals, mp. 149-152°.

Calcd. for $C_{20}H_{21}NO_7S_2$: C, 53.20; H, 4.69; N, 3.10; S, 14.20.
Found: C, 53.45; H, 4.60; N, 3.09; S, 13.99.
MW (osmometric), 436; Calcd., 419.5.

4-Hydroxy-2-thiono-1,2-dihydro-quinoline-3-carboxylic acid(V).

A solution of 0.7 g. (2.8 mmoles) of III in 3 ml. water, 0.3 g. NaOH and 100 ml. of DMF is heated to 100° for 6 hrs. The solvent is removed, the residue treated with water and filtered. After acidification with HCl, 0.2 g. of V is obtained as yellow prisms from ethanol, mp. 295°.

Calcd. for $C_{10}H_7NO_3S$: C, 54.29; H, 3.19; N, 6.33; S, 14.49.
Found: C, 54.18; H, 3.28; N, 6.29; S, 14.61.

Methanetricarboxylic acid dianilide thioanilide(VI).

Procedure a. To a mixture of 2.3 g. (100 mg.-atoms) of sodium in 300 ml. of THF, 25.4 g. (100 mmoles) malonic acid dianilide is added and heated for 8 hrs. The solution is cooled in an ice bath and then 13.5 g. (100 mmoles) phenyl-isothiocyanate is added. After the addition, the reaction mixture is heated for 2 hrs. Acidification with dil. HCl yields a small amount of methanetricarboxylic acid trianilide which is removed by filtration. Ether is then added to the oily layer which is separated from the aqueous phase. The precipitated solid is filtered and crystallized from ethanol to give 33.6 g. (80%) of VI, mp. 205-206°.

Procedure b. When a mixture of 4 g. (13.5 mmoles) of I is heated to reflux with 5 ml. (54 mmoles) of aniline for 30 min., 4.2 g. (80%) of VI is obtained in pure state after washing with ether.

Calcd. for $C_{22}H_{19}N_3O_2S$: C, 67.85; H, 4.92; N, 10.79; S, 8.23.
Found: C, 68.09; H, 5.03; N, 10.65; S, 8.19.

REFERENCES

1. E. Ziegler, H. Junek, A. Metallidis and H. Binder, Monats. Chem., 98, 2242 (1967)
2. E. Ziegler, H. Junek and A. Metallidis, ibid., 101, 92 (1970).
3. A. Michael, J. Prakt. Chem., 35, 450 (1887).
4. G. Barnikow and H. Kunzek, Ann., 700, 36 (1966).

5. E. Ziegler, "Zur Chemie der Ketene," Chimia, 24, 62 (1970).

6. S. Ruhemann, J. Chem. Soc., 93, 621 (1908).

7. D. E. Worrall, J. Am. Chem. Soc., 40, 415 (1918).

(Received December 18, 1969)