Tetrahedron Letters No.4, pp. 323-324, 1971. Pergamon Press. Printed in Great Britain.

THE THERMOLYSIS OF TRIALKYLAMINE CARBOETHOXYIMIDE

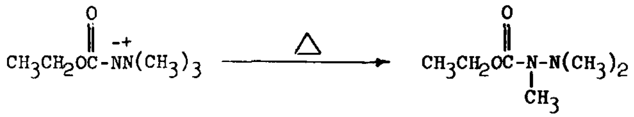
Edward A. Sedor

Ashland Chemical Co., Bloomington, Minnesota 55420

(Received in USA 17 December 1970; received in UK for publication 24 December 1970)

Azido formates have been studied rather extensively and are reported to undergo photolytic Curtius rearrangements[1] and thermal and photolytic decompositions, producing carboethoxynitrenes[2]. Lwowski has shown that the azide ($\mathrm{CH_3CH_2OCON_3}$), photolytically rearranged at low temperatures and in methanol to give ethoxy isocyanate ($\mathrm{CH_3CH_2\text{-}ONCO}$)[1]. Also thermal or photolytic decomposition in aprotic solvent yielded carboethoxy nitrenes[2]. Because the acyl aminimides ($\mathrm{RCO\overset{-}{N}\overset{+}{N}R_1R_2R_3}$) are reported to undergo thermal Curtius type rearrangements, yielding isocyanate and amine ($\mathrm{RNCO + NR_1R_2R_3}$)[3], our interest was aroused as to the possible rearrangement of trimethyl amine carboethoxyimide (I) ($\mathrm{CH_3CH_2OCO\overset{-}{N}\overset{+}{N}(CH_3)_3}$)[4].

We studied the thermolysis at 175° of (I) in diglyme-cyclohexane (sealed tube), cyclohexane (sealed tube) and neat, and we found that the reaction differed from that of the azide. The thermolysis gave no isocyanate, carbamate or N-cyclohexyl ethyl carbamate-products expected from either a Curtius type rearrangement or products derived from carboethoxynitrene. In all three cases, only one major product was found, 1,2,2-trimethyl-1-carboethoxyhydrazine - the product from methyl group migration. Here was an example of a "Wawzonek rearrangement"[5], a Stevens rearrangement involving an aminimide. Although Wadsworth[6] has reported a methyl group migration for a cyclic aminimide, this is the first reported methyl group migration for a non-cyclic aminimide.



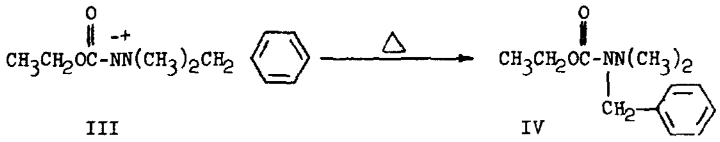
$$\mathrm{CH_3CH_2O\overset{\overset{O}{\|}}{C}\text{-}\overset{-}{N}\overset{+}{N}(CH_3)_3 \xrightarrow{\Delta} CH_3CH_2O\overset{\overset{O}{\|}}{C}\text{-}\underset{\underset{CH_3}{|}}{N}\text{-}N(CH_3)_2}$$

I II

The yield of II was 75%, bp 160-162°/760mm and was identical with II prepared from ethyl chloroformate and 1,2,2-trimethylhydrazine as determined by ir, nmr and elemental analysis.

In Wawzonek's report[5] the thermolysis was carried out using a 1,1-dimethyl-1-benzyl-2-

acetimide with exclusive benzyl N-N migration. We thermolyzed III to determine if competitive group migration would occur. As should be expected, the more electrophilic benzyl group



III IV

migrated exclusively (82%) with structure proof for IV provided by ir, nmr and elemental analysis.

When I was photolyzed in methanol or methanol-cyclohexane for up to 96 hours, only starting material was recovered with less than 1% unidentified dark material.

Further studies on the rearrangement of amine formimides are in progress.

REFERENCES

1) W. Lwowski, R. DeMauriac, T. W. Mattingly and E. Schieffele, Tetrahedron Letters, 1964 3285.

2) W. Lwowski and T. W. Mattingly, J. Amer. Chem. Soc., 87 1947 (1965) and references cited in this paper.

3) R. F. Smith and P. C. Briggs, Chem. Commun. 1965, 120; M. S. Gibson and A. W. Murray, J. Chem. Soc., 1965, 880; S. Wawzonek and R. C. Gueldner, J. Org. Chem., 30 3031 (1965); W. J. McKillip, L. M. Clemens and R. Haugland, Can. J. Chem., 45, 2613 (1967); R. C. Slagel and A. E. Bloomquist, Can. J. Chem., 45, 2625 (1967); B. M. Culbertson, E. A. Sedor and R. C. Slagel, Macromolecues 1 254 (1968).

4) M. S. Brown, J. Chem. Eng. Data, 12 612 (1967) reports mp 95-98° (sublimed 80°/0.1 mm); our sample mp 94.5° (sublimed 80°/0.1 mm).

5) S. Wawzonek and E. Yeakey, J. Amer. Chem. Soc., 82 5718 (1960).

6) W. S. Wadsworth and W. D. Emmons, J. Org. Chem., 32 1270 (1967).