

Formation of Urea in Thermal Decomposition of Dimethyl-
or Diethyl-cinnamylamine Oxide

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Thermal decomposition of t-amine oxide is well known reaction which may be classified (1) into (a) Meisenheimer rearrangement giving dialkylalkoxyamine, (b) Hofmann-type elimination giving olefin and hydroxylamine, (c) reduction to t-amine by oxidizable compound and (d) dehydration (2). In the case of t-amine oxides bearing allyl or benzyl group, Meisenheimer rearrangement takes place almost exclusively. For benzyldialkylamine oxide, a mechanism involving free radical cleavage of N-C bond was presented (3) while for allyldialkylamine oxide, a cyclic transition state was assumed (4). Our preliminary kinetic investigation of the rearrangement of allyldialkylamine oxide revealed that the reaction had typical characteristics of the free radical reaction (5).

The characteristics of induced reaction is shown for triallylamine oxide in Fig. 1. In every measurement of most of t-amine oxide bearing allyl group, an abrupt increase in rate was observed although the exact value of induction period was not reproducible. That the abrupt increase can not be ascribed to common successive reaction was ascertained by calculation (5). Similar induction period was also observed in rearrangement of the isolated amine oxides. The addition of n-butyl mercaptane caused a nearly complete inhibition of alkoxyamine formation and only slow formation of the amine and the disulfide was observed. The latter resulted from normal oxidation reaction but a remarkable inhibition indicated that the rearrangement involved a radical chain mechanism. From these observations, it was concluded that even in Meisenheimer rearrangement of t-amine oxide bearing allyl group, the free radical (chain) reaction was involved.

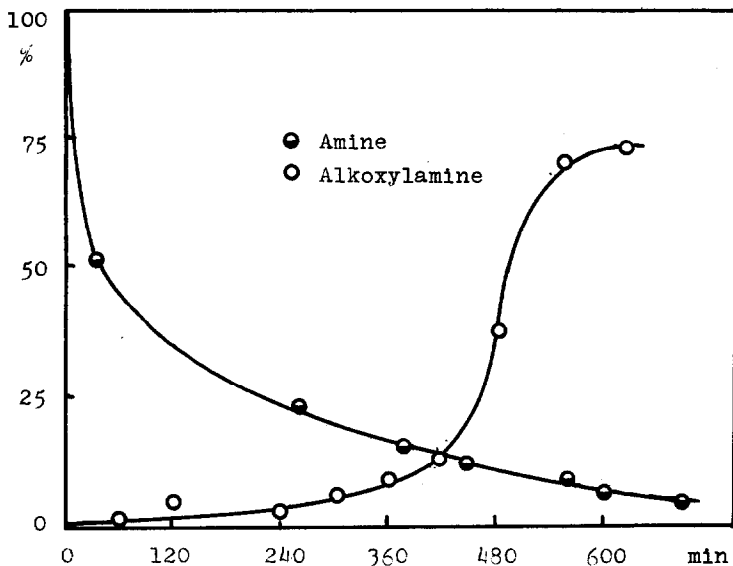
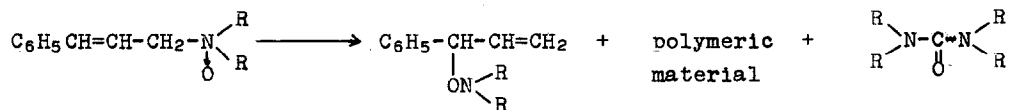


Fig.1 Alkaline Hydrogen Peroxide Oxidation of Triallylamine.
Change in concentration of the amine and the alkoxy-
amine (60°C in methanol)

Now the authors wish to report the novel pattern of thermal decomposition of *t*-amine oxide bearing cinnamyl group. Dimethylcinnamylamine oxide gave tetramethylurea (17.2% based on the amine used) together with the normal Meisenheimer product, dimethyl(1-phenyl- Δ^2 -propenyloxy)amine (16.9% based on the amine used) (6). There were several minor products. Formation of the urea may be considered to result from the attack of aminoxyl radical to allylic methylene but not to double bond. But the mechanism of the reaction was not yet clear. Similarly, diethylcinnamylamine oxide gave tetraethylurea in a comparable yield to the dimethyl homolog.



R=CH₃, C₂H₅

0.10 mole of peroxybenzoic acid in ca. 300 ml of chloroform was added dropwise into 0.1 mole of dimethylcinnamylamine during 2.5 hours at room temperature and the resultant solution was stirred for additional 2 hours. The solution was extracted with 25 ml of water three times. The combined aqueous solution was extracted with 25 ml of chloroform. Into the aqueous solution was dissolved 7.5 g of sodium hydroxide and the solution was heated at 80°C for 48 hours. After cooling, 10 N sodium hydroxide solution was added into the solution until no more amine or alkoxyamine separated, and the mixture was extracted with ether several times. The ether layer was dried on anhydrous sodium sulfate and after evaporation of ether, two major fractions were obtained on distillation.

The low boiling fraction (64°C at 25 mmHg) was found to be tetramethylurea by the following observations. NMR absorption (in CCl_4) δ 7.29 τ singlet only. IR absorption at 1630 cm^{-1} . VPC identity with the authentic tetramethylurea. That tetramethylurea was formed as a primary product (not from secondary reaction) was ascertained by observed monotonous increase in its concentration during the rearrangement. Tetraethylurea from dimethylcinnamylamine oxide was identified with that from relevant synthesis (diethylamine and phosgen). The high boiling fraction (130-135°C at 1 mmHg) was hydrolyzed in the presence of hydrochloric acid, giving dimethylamine (identified as HCl salt) and a small amount of carbonyl compound which was identified (by VPC) with phenyl vinyl ketone from relevant synthesis (7). Neither cinnamaldehyde nor cinnamic acid was detected. Thus the high boiling fraction was determined to be the normal Meisenheimer product, dimethyl(1-phenyl- Δ^2 -propenyloxy)amine.

References

1. Classification into (a)-(c) was made elsewhere : R.Kreher, Tetrahedron Letters, 2591 (1966).
2. J.Thesing, Ann. Chem., 671, 119 (1964).
3. U.Schöllkopf, M.Patsch and H.Schäfer, Tetrahedron Letters, 2515 (1964).
4. R.F.Kleinschmidt and A.C.Cope, J. Am. Chem. Soc., 66, 1929 (1944).
5. Detailed description on the Kinetics will be presented in a separate paper.
6. Rearrangement was observed to be considerably fast and during oxidation an

appreciable amount of the dialkylalkoxamine was formed. Water extraction collected the amine oxide in 60-70% on the basis of the amine used.

7. The ketone was unstable in the condition, giving a polymeric material.