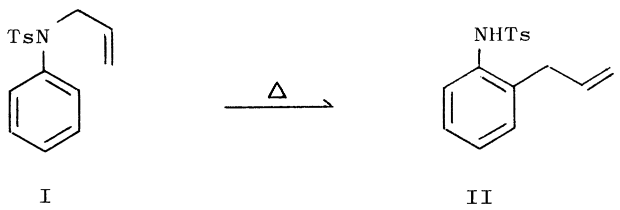
CHEMISTRY LETTERS, pp. 1213-1216, 1973. Published by the Chemical Society of Japan

THE AMIDE-CLAISEN REARRANGEMENT. III.
THE THERMAL REARRANGEMENT OF N-ALLYL-N-TOSYLANILINE

Seisaku INADA, Syuhei IKADO, and Mitsuo OKAZAKI
Department of Chemical Engineering, Faculty of Engineering,
Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152

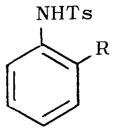
The use of a small amount of triphenylphosphine in the thermal rearrangement of N-allyl-N-tosylaniline to 2-allyl-N-tosylaniline in N,N-dibutylaniline depressed, to a great extent, the decomposition of the reaction mixture. The sum of the yields of rearrangement products, which were 2-allyl- and 2-(trans-1-propenyl)-N-tosylaniline, and 2-methyl-1-tosylindoline, reached to 85%.

Carnahan and Hurd[1)] showed that the thermal treatment of N-allyl-N-tosylaniline (I) at 300°C brought about evolution of hydrogen sulfide and resin formation, with only traces of primary amine derivatives formed. We also reported[2)] that I gave crude 2-allyl-N-tosylaniline (II) only in 15% yield,[3)] when heated at 230°C for ten hours in a nitrogen atmosphere, and further heating caused the decomposition of the reaction mixture to resinous matters, although N-allyl-N-tosyl derivatives of 1- and 2-naphthylamine rearranged, in a shorter reaction time, to the corresponding Claisen-type rearrangement products in >90% yields, respectively.[2)]

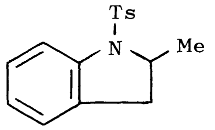


It has now been found, however, that the thermal rearrangement of I in N,N-dibutylaniline proceeds smoothly and the decomposition is largely depressed, especially when a small amount of triphenylphosphine is added to the solution.

Thus, when 2.00g of I was heated in 10 ml of N,N-dibutylaniline containing 0.20g of triphenylphosphine at 245°C for 55 hours in a nitrogen atmosphere, II,[4] 2-methyl-1-tosylindoline[4] (V), 2-(trans-1-propenyl)-N-tosylaniline[4] (III), and N-tosylaniline (IV) were obtained in 73, 11, 1, and 1% yields, respectively, with 10% recovery of I. Accordingly, the yield of rearrangement products (II, III, and V) sums to 85%.[5]



III R: $CH=CHCH_3$
IV R: H



V

In order to assess the effectiveness of the addition of triphenylphosphine, I was heated in N,N-dibutylaniline in the presence or absence of triphenylphosphine at 260°C. The yield of II was determined spectrophotometrically, after extraction of alkali-soluble matters (II, III, and IV) from the reaction mixture, followed by separation of them by tlc. The results are shown in Fig. 1. In the absence of triphenylphosphine, the maximum yield of II was 42% (12 hours) and, on further heating, the yields decreased rapidly with increasing reaction time. This exhibits the relatively violent decomposition of the reaction mixture to occur.[6] In the presence of triphenylphosphine, on the other hand, the maximum yield of II reached to 61% in 19 hours, and the decomposition also took place more mildly. It is now clear that the presence of triphenylphosphine in thermal rearrangement of I to II in N,N-dibutylaniline is very effective to inhibit the decomposition of the reaction mixture.

We examined the effect of several solvents, i.e., tetralin, diphenyl ether, diethanolamine, ethylene glycol, carbitol, and N,N-bis(β-hydroxyethyl)aniline. When I was heated in these solvents at 245°C or below, the reaction mixture turned gradually brown and were led to dark resinous matters within a few hours of reaction. They were not sufficient to depress the decomposition. N,N-Dibutylaniline described above has been proved to be the best solvent, in which such a polymerization in a shorter reaction time could not be observed. It is known that, in the Claisen rearrangement of allyl phenyl ethers, N,N-dialkylanilines are effective solvents to prevent the decomposition of the reaction mixture.[7] This is also the case in the amide-Claisen rearrangement of I to II.

In the previous paper,[8] we showed that the presence of atmospheric oxygen

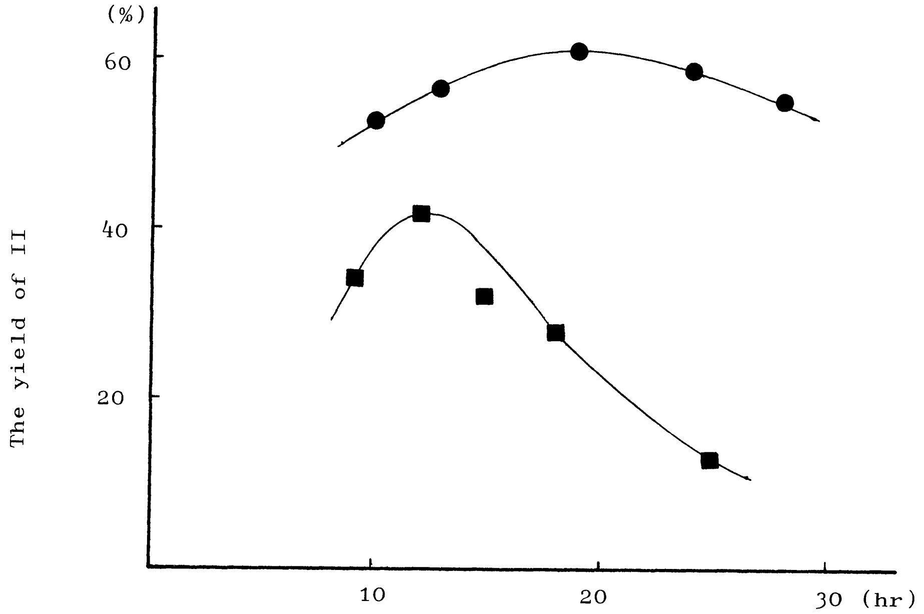
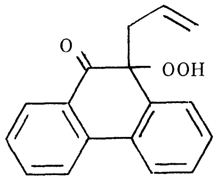


Fig. 1. Effect of the addition of triphenylphosphine in the rearrangement of I to II in N,N-dibutylaniline

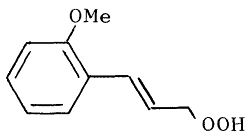
● In the presence of triphenylphosphine

■ In the absence of triphenylphosphine

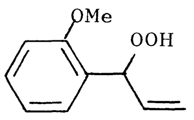
promoted the decomposition of the reaction mixture to resinous matters in the amide-Claisen rearrangement of 4-(N-allyl-N-tosylamino)naphthal-N-methylimide to 3-allyl-4-(N-tosylamino)naphthal-N-methylimide. And, in the present study, triphenylphosphine oxide was detected by tlc,9) the formation of which might suggest that hydroperoxides were formed from the allylic compound II. It is known that the Claisen rearrangement product affords hydroperoxides which may be radical initiators. Marcinkiewicz and his coworkers10) showed that hydroperoxide VI was easily formed from 10-allyl-9-phenanthrol during its purification. Chirko et al.11) also obtained hydroperoxides VII and VIII in a few percent yields, respectively, by the autoxidation of o-allylanisole. From these, it may be considered that triphenylphosphine reduces hydroperoxides formed during the reaction to more



VI



VII



VIII

stable species, and excludes the decomposition of the reaction mixture caused by them.

In conclusion, the additive effect of triphenylphosphine to solvent effect of N,N-dibutylaniline toward the decomposition made possible the novel rearrangement of I to II, which is useful for the practical synthesis of the latter.

REFERENCES AND NOTES

1) F. L. Carnahan and C. D. Hurd, J. Amer. Chem. Soc., 52, 4588 (1930).

2) S. Inada, F. Hojo, S. Tanaka, and M. Okazaki, The 28th Autumn Annual Meeting of the Chemical Society of Japan, Nagoya, 1972. Abst. Papers, I, p. 430.

3) contaminated with III and IV.

4) II, III, and V are new compounds. II. mp 70.5-71°C. Found: C, 66.93; H, 5.83; N, 4.87%. Calcd. for $C_{16}H_{17}NO_2S$: C, 66.87; H, 5.96; N, 4.87%. III. mp 134-134.5°C. Found: C, 67.07; H, 5.85, N, 5.07%. Calcd. for $C_{16}H_{17}NO_2S$: C, 66.87; H, 5.96; N, 4.87%. V. mp 63.5-64.5°C. Found: C, 67.17; H, 5.90; N, 4.98%. Calcd. for $C_{16}H_{17}NO_2S$: C, 66.87; H, 5.96; N, 4.87%. The structures of all these compounds were supported by satisfactory spectral data.

5) 94%, based on recovered I.

6) In the previous study$^{8)}$ on the rearrangement of 4-(N-allyl-N-tosylamino)-naphthal-N-methylimide to 3-allyl-4-(N-tosylamino)naphthal-N-methylimide, we observed that the amounts of tars increased with decreasing the yields of the rearrangement product during the decomposition.

7) A.Jefferson and F.Scheinmann, Quart. Rev.(London), 22, 419 (1968): D.S.Tarbell, "Organic Reactions", Vol. 2, John Wiley & Sons, Inc., New York, p.24 (1944).

8) S.Inada, A.Arikawa, and M.Okazaki, Yuki Gosei Kagaku Kyokai Shi, 31, 598 (1973).

9) Triphenylphosphine oxide was prepared according to the Michaelis and Cleichmann's method. A. Michaelis and L. Gleichmann, Ber., 15, 801 (1882). A component in the reaction mixture had the same R_f values with this compound on silica gel layers when developed with benzene, benzene-acetone (9:1), and ethyl acetate.

10) S. Marcinkiewicz, J. Green, and P. Mamalis, Tetrahedron, 14, 218 (1961).

11) A. I. Chirko, I. G. Tischenko, and V. V. Filitovich, Zh. Org. Khim., 7, 130 (1971); Chem. Abstr., 74, 99555x (1971).

(Received September 8, 1973)