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TRANSANNULAR REACTIONS ON 6,11-DIHYDRODIBENZO[b,e]THIEPINS

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Novel two types of transannular reaction of 6,11-dihydrodibenzo[b,e]thiepins have been reported. The reactions between 11-methoxy-11-phenyl-6,11-dihydrodibenzo-[b,e]thiepin 5-oxide (I) or 11-phenyl-6,11-dihydrodibenzo[b,e]thiepin-11-ol 5-oxide (II) and $SbCl_5$ in CH_2Cl_2 generated a stable dark green solution. With basic hydrolysis of this solution, 6,11-epoxy-11-phenyl-6,11-dihydrodibenzo[b,e]thiepin (III;mp142°) was given obtained in 88-93% yield.

The reactions of I or II with 70% $HClO_4$ gave another transannular product, 5,11-epoxy-11-phenyl-6,11-dihydrodibenzo[b,e]thiepinium perchlorate (IV); mp221° (decomp.), in good yield. When IV was hydrolyzed in alkaline solution or recrystallization from EtOH, IV migrated readily to give III *via* Stevens type rearrangement.

On the other hand, transannular products were obtained even by the reaction of 6-methoxy-6,11-dihydrodibenzo[b,e]thiepin-11-one (V) with Grignard reagents (R'MgX; $R'=CH_3$, Ph), and also that of 11-methyl-, 11-phenyl-, and other 11-substituted 6,11-dihydrodibenzo[b,e]thiepin-11-ols with N-chlorosuccinimide.