NOVEL BICYCLOANNULATION VIA TANDEM VINYLATION AND INTRAMOLECULAR DIELS-ALDER REACTION OF FIVE-MEMBERED HETEROCYCLES

Kenji Hayakawa, Mitsuaki Yodo, Satoru Ohsuki, and Ken Kanematsu*
Institute of Synthetic Organic Chemistry, Faculty of Pharmaceutical
Scieneces, Kyushu University 62, Higashi-ku, Fukuoka 812, Japan

Trans-4-(phenylsulfinyl)-3-buten-2-one (1) was found to undergo a new versatile addition-elimination reaction with five-membered heterocyclic compounds such as furans, pyrroles, imidazole, pyrazole, and 6-dimethylaminofulvene to give an excellent yield of corresponding trans-4-aryl-3-buten-2-ones (2). The intramolecular Diels-Alder reaction of propargyl ethers 3, prepared from 2 by successive reduction and propargylation, has been investigated. While the thermal reaction of $\underline{3}$ afforded cycloadducts $\underline{4}$ in moderate yields, treatment of $\underline{3}$ with t-BuOK in refluxing t-BuOH gave another type of adducts 6 via allenyl ethers 5 in almost quantitative yields. This bicycloannulation strategy was successfully applied to a new synthesis of psoralen which is of current interest due to the unique photoreactivity with DNA. The acid-catalyzed reaction of sulfoxide 7 with furan gave 8 in 78% yield. The intramolecular Diels-Alder reaction of the neopentylacetal of $\underline{8}$ in the presence of Pd/C followed by acid-hydrolysis afforded the tricyclic ketone 9 in 38% overall yield. Baeyer-Villiger oxidation and dehydrogenation of 9 completed the synthesis of psoralen (10). The hitherto unknown azapsoralen $\underline{11}$ was also synthesized by this method.

Phosing
$$\frac{10}{2}$$
 $\frac{10}{8}$ $\frac{10}{2}$ $\frac{10}{11}$ $\frac{10}{2}$ $\frac{10}{11}$ $\frac{10}{2}$ $\frac{10}{11}$ $\frac{10}{2}$ $\frac{10}{11}$ $\frac{10}{2}$ $\frac{10}{11}$ $\frac{10}{2}$ $\frac{10}{2$