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

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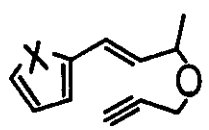
Trans-4-(phenylsulfinyl)-3-buten-2-one (1) was found to undergo a new versatile addition-elimination reaction with five-membered heterocyclic compounds such as furans, pyrroles, imidazole, pyrazole, and 6-dimethylaminofulvene to give an excellent yield of corresponding trans-4-aryl-3-buten-2-ones (2). 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 3 afforded cycloadducts 4 in moderate yields, treatment of 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 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 11 was also synthesized by this method.



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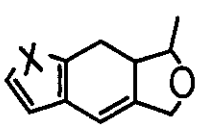

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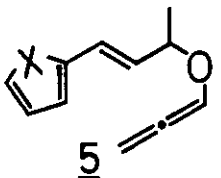

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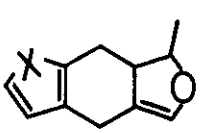

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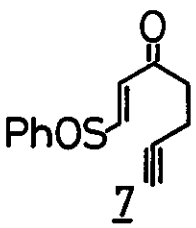

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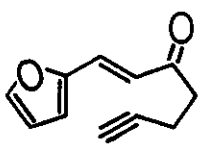

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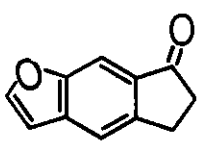

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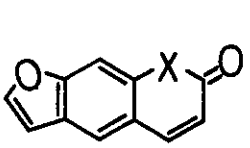

10, X=O
11, X=NH