SYNTHESIS AND CYCLOADDITION REACTION OF 1,2-AROMATIC RING FUSED-3-CYANO-INDOLIZINES

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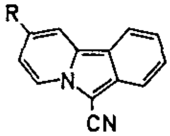
Bicyclic nitrogen containing heterocycles like indolizines and azapentalenes whose resonance hybrids involve an ylid structure could serve as a dipolar bicycloimmonium ylid. Therefore, annulation of carbo- or hetero-aromatic nucleus to indolizine at 1,2-positions is expected to activate 3-cyanoindolizines by means of aromatic stabilization in favor of azomethine ylid structure. Thus, 6-cyanobenzo[c]pyrrolo[1,2-a]pyridines (2) was prepared by 1,3-dipolar cycloaddition of pyridinium dicyanomethylids (1) onto benzyne. (2) readily underwent cycloaddition with dibenzoyl acetylene to give the corresponding 1,2-benzocycl[2.2.3]azines (3) in good yields. Treatment of (3) with P_4S_{10} in pyridine produced a new nonclassical thiophene system (4). This system was almost inert to dimethyl acetylenedicarboxylate (DMAD), thus (5) being assumed to be a major contributor to the ground state. Reaction of pyridinium ylids (1) with dibenzoyl acetylene afforded the 1,2-dibenzoyl-3-cyanoindolizines (6), treatment of which with hydrazine gave the corresponding ring fused pyridazines (7). The pyridazine (7a: R=H) with DMAD produced the 1:2 adduct, whose structure is supposed to be (8). P_4S_{10} treatment of (6a: R=H) in refluxing pyridine gave a new nonclassical thiophene (9) albeit only in 3 % yield. DMAD underwent cycloaddition with (9) in refluxing toluene to afford the dehydrogenated 1:2 adduct (10) along with a trace amount of (11).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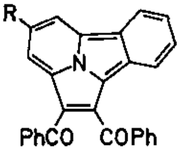
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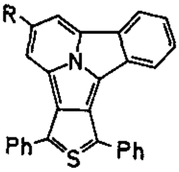
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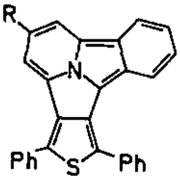
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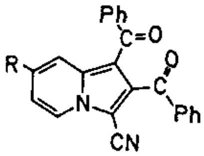
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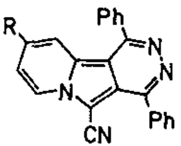
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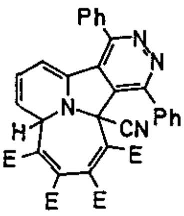
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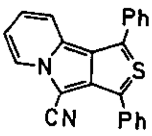
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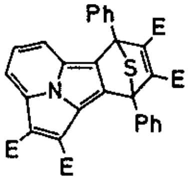
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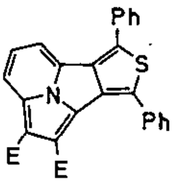
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