HIGH-PRESSURE CYCLOADDITION OF AZA-AROMATIC COMPOUNDS

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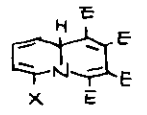
2-Bromo-, 2-chloro-, 2-cyano-, and 2-fluoro-pyridines, whose nucleophilicities are not high enough for them to attack dimethyl acetylenedicarboxylate (DMAD) at atmospheric pressure, react with the latter under high-pressure (10 kbar) at room temperature to give 1:2 adducts (1) and (2) (from the bromo-, chloro-, and cyano-pyridines) or a 1:3 adduct (3) (from the fluoro-pyridine).

Indoles react rather slowly with DMAD, for example 112 days at room temperature to give a variety of compounds. In the high-pressure reaction (10 kbar) of indole with DMAD for 1 week, the dihydrocarbazole (4) in which three molecules of DMAD are incorporated was of major product. The new product (5) was also isolated in the case of reaction at 10 kbar for 24 h. The reaction of N-methylindole with DMAD at 10 kbar at room temperature for 1 week gave the benzazepine (6) in 20 % yield which is better than that under atmospheric condition reported.

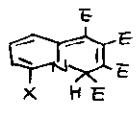
4-Ethoxy-8-methylquinazoline which did not react with DMAD at atmospheric pressure because of steric hindrance reacted at 10 kbar to produce the rearranged 1:2 adduct (7) in 34 % yield.

Reaction of DMAD with a variety of 2(1H)-pyridones (8) at 10-15 kbar pressure and 60-70 °C gives the bicyclic adducts (9), some of which are unobtainable under atmospheric pressure in moderate yields.

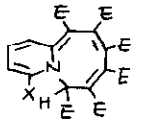
($E = COOCH_3$)



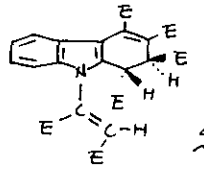
1 ($X = Br$)



2 ($X = Br, Cl, CN$)



3 ($X = F$)



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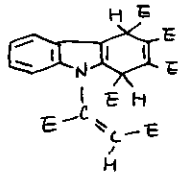

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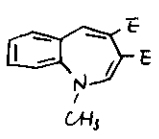

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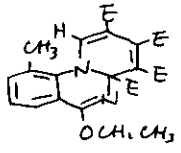

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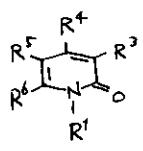

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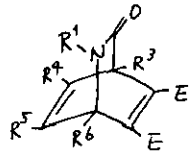

9