RING-ENLARGEMENT REACTIONS OF BENZENE DERIVATIVES WITH ALKOXYCARBONYLNITRENE

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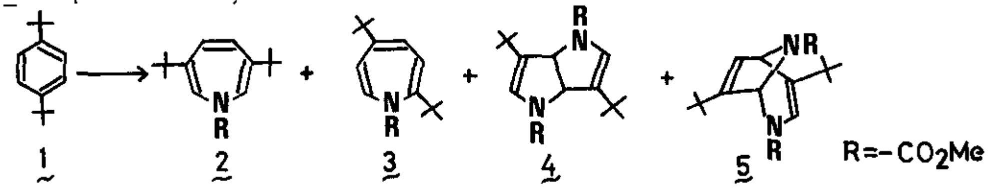
Thermal reactions of methyl azidoformate with 1,4-di-tert-butylbenzene(1) were investigated. We report first the formation of 1H-azepines(2 and 3) and dinitrogenated products(4 and 5) as well as the reaction mechanism for these products. The reaction mixture that was obtained by heating 1 and methyl azidoformate at 125°C for 3 hrs was separated by means of preparative low pressure liquid chromatography to give 2,3,4 and 5 in 8.2,5.8,17.7 and 8.8% yield respectively, and another unknown product. The dinitrogenated product 4 could also be derived from 2 in 25% yield by heating with methyl azidoformate, but not from 3. In addition, heating of 5 at 230°C for 6 hrs led to 4 in quantitative yield.



Dehydrogenation of 4 and decarbonylation of 4 and its dehydrogenated product 6 were studied to gain insight into the properties of pyrrolo[3,2-b]pyrrole derivatives. Heating of 4 with DDQ produced 6 in quantitative yield. When 7 or 4 was treated with KOH in ethanol at room temperature or at 50°C, decarbonylation partially occured to afford mono methoxycarbonyl derivative 7 or 8 in 96 or 55% yields. On the other hand, refluxing 4 with alcoholic-KOH produced pyrrole derivative 9 in 68% yield.