Synthesis of Piperitenone by the Condensation of Mesityl Oxide with 4-Diethylaminobutanone-(2) in the Presence of Triton-B

Sir:

Recently, Bergmann and Bracha¹⁾ has published the synthesis of piperitenone (I) involving the condensation of mesityl oxide (II) with methylvinylketone (III) in the presence of sodium *t*-pentoxide in toluene. However, Naves and Conia^{2,3)} proved that the only product formed under the described condition was the well-known self-condensation product of II, viz. isoxylitones (IV)⁴⁾. Thereafter, these workers^{5,6)} and Ueda⁷⁾ concluded that the product contained I in a small amount (below 8 %) together with IV. Wiemann⁸⁾ has also prepared I in a yield of 15 % by the condensation of II with III in the presence of barium oxide in boiling benzene.

These reported results show that the ratio of I and IV in the reaction products may vary due to slight differences in operating condition, and the advantage using strong base or high reaction temperature to maintain a reasonable carbanion concentration of II may be offset by greater losses due to polymerization of a sensitive reagent such as III.

In this paper, we propose a new procedure for condensation of II with 4-diethylaminobutanone-(2) (V) instead of III in the presence of Triton-B (trimethylbenzylammonium hydroxide in ethanol) in ether. This gave more satisfactory result than the previous methods and the yield of I could be brought up to 50.3 % on the basis of V used.

To a gently boiling solution of 49 g (0.5 moles) of II and 0.015 moles of Triton-B (15

% ethanol solution) in 100 ml of ether, a solution of 14.3 g (0.1 mol) of V in 40 ml of ether was added dropwise over a period of one hour with stirring in the current of nitrogen. The mixture was refluxed for one hour, and then poured into water containing 10 ml of glacial acetic acid. The organic layer washed, dried, and evaporated. The residue was distilled under reduced pressure to give 8.6 g of oily product; b. p. 110~128°/8 mm Hg, $\lambda_{\text{max}}^{\text{MeOH}}$ 243 m μ (ϵ 9,320), 278 m μ (ϵ 7,200). The product was confirmed to contain 87.8 % of I by gaschromatographic analysis, and gave anti- and syn-form 2,4-dinitrophenylhydrazones, m. p. 184~184.5°C and 135°C, respectively, which showed no depression on admixture with authentic samples.

The various reaction conditions examined by the present authors for the condensation of II with V and corresponding yields were as follows; (a) with potassium *t*-butoxide (0.18 equiv.), 0.8 % (main product was IV), (b) with potassium hydroxide (0.15 equiv.) in benzene, 23.9 %, (c) with potassium ethoxide (0.18 equiv.) in ethanol, 12.8 %, (d) with Triton-B (0.15 equiv.) in dimethylsulfoxide, 0 % (main product was IV), (f) on use of II instead of V with Triton-B in ether, 40.2 %.

Survey of the above-mentioned results indicated that release of III from V in high local concentration at the surface of the insoluble basic catalyst will promote polymerization, while the use of homogeneous reaction system appears to be a more important factor.

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