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REACTION OF ENAMINES WITH γ-BROMO-αβ-UNSATURATED ESTERS

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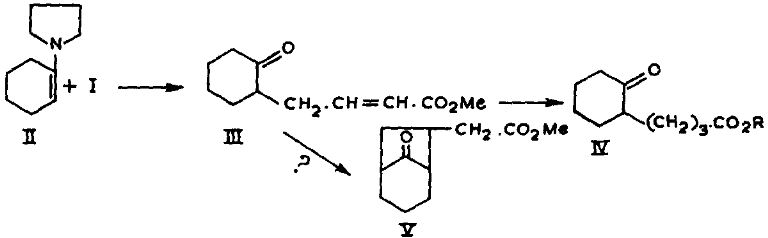
Since enamines have been shown to react with allyl halides, α-haloesters and αβ-unsaturated esters[1], it was of interest to see how they would behave with γ-bromo-αβ-unsaturated esters. The author is not aware of any attempt made in this direction.

As a model study methyl γ-bromocrotonate (I) was allowed to react with cyclohexanone enamines (II) in benzene under refluxing condition. After usual hydrolysis and workup, a liquid material boiling at 118-122°/0.4 mm was isolated in 52 per cent yield as the main product[2] of the reaction. The homogeneous character of the material was established from TLC and the structure has been confirmed to be the normal alkylation product (III) for the following reasons:



1. The compound contained no bromine and did not produce any colouration with tetranitromethane.

2. It showed UV absorption at 212 mμ(ϵ 10,230) and 288 mμ (ϵ 112) in ethanol, infra-red (CCl_4) bands at 1722 (strong and broad) and 1670 cm^{-1} (medium) characteristics of α,β-unsaturated ester.

3. It furnished DNP (MeOH-EtoAc), m.p. 146-147°, $\lambda_{max}^{CHCl_3}$ 365 mμ(ϵ 24120) and semicarbazone (MeOH), m.p. 169-170° in very low yields.

4. On catalytic reduction (Pd-C), the compound absorbed one mole of hydrogen per mole to give only the saturated ester (IV, R=Me), λ_{max}^{EtOH} 283 mμ(ϵ 42), strong infra-red (CCl_4) bands at 1745 and 1720 cm^{-1}. This reduced ester produced a DNP (MeOH), m.p. 112° in quantitative yield.

5. The ester (IV, R=Me) on acid or alkaline hydrolysis afforded the keto acid (IV, R=H), m.p. 60-61° (reported[3] m.p. 60-61°), semicarbazone m.p. 185-187° (reported[3] m.p. 185-187°) alone or mixed with authentic samples.

It is interesting to note that the ester (IV, R=Me) on acid hydrolysis did not suffer any molecular rearrangement[4] characteristic of some ϵ-keto acids reported by Herz[5] and Banerjee[6].

The carbonyl band of (III) near 288 mμ is significantly intense (see above) than the value expected for normal carbonyl group. This may possibly be due to some type of intramolecular exchange interaction reaction[7] between the C=O and the double bond in the compound (III); geometrical condition for this interaction may be satisfied only by the axial orientation of the side chain. The C=O in (III) is definitely hindered (very poor yields of DNP and semicarbazone) but the double bond behaves normally at least on catalytic hydrogenation.

Studies are now in progress with enamines of other ring systems and γ-bromo-$\alpha\beta$-unsaturated esters of different steric considerations. The transformation of the compound of the type (III) to the bicyclo octane system (V) is also under investigation.

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