A New Azepine and Azepinone Synthesis

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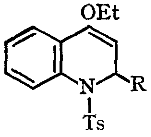
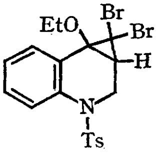
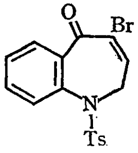
IN azatropone syntheses the main problems have been dehydrogenating the intermediates and preventing dimerisation of the products.[1,2] To avoid these difficulties a new synthesis is needed.



(I)



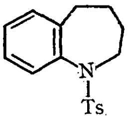
(II)



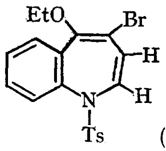
(III)

Ts = toluene-*p*-sulphonate

The enol-ether (I; R = H) (m.p. 87°)† and dibromo-carbene (from $PhHgCBr_3$ [3] or $CHBr_3$ and NaOBu^t)[4] yielded the dibromocyclopropane (II) (m.p. 131°) which reacted with silver nitrate in aqueous ethanol[5] to give, in 20% yield, a substance $C_{17}H_{14}BrO_3NS$ (m.p. 168°) which we regard



(IV)



(V)

as (III). The latter (ν_{max} 1665 cm.$^{-1}$) has an n.m.r. spectrum consisting of a multiplet from τ2·05 to 3·0 (8 aryl and 1 olefin H), a doublet at

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† Satisfactory analytical and mass spectrographic data were obtained for all new compounds.

τ 5·4 (J 5·5 c./sec., 2 methylene H), and a singlet at τ 7·58 (3 methyl H); on catalytic hydrogenation it gave the tetrahydro-compound (IV) identical to that obtained from known materials by conventional procedures.

When heated under reflux in pyridine,[4] (II) gave in 35% yield a product (m.p. 98°) ($C_{19}H_{18}BrO_3NS$) to which we allocate the predicted structure (V). The n.m.r. spectrum of the latter was diagnostic, consisting of the following signals: multiplet from τ 2·2 to 2·95 (8 aryl H), a quartet at τ 3·8 (J 7 c./sec., 2 olefin H), a blurred sextuplet at τ 6·8 (2 methylene H in nonequivalent magnetic environment[7]), a singlet at τ 7·62 (3 methyl H), Somewhat unexpectedly, compound (V) was unaffected by mild acid treatment.

This synthesis satisfies both criteria that we have laid down; thus it circumvents dehydrogenation problems and also will allow introduction of blocking groups by employing suitable substituted starting materials [*e.g.* (I; R = Me)] the precursors of which are to be found in the literature.[8]

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