

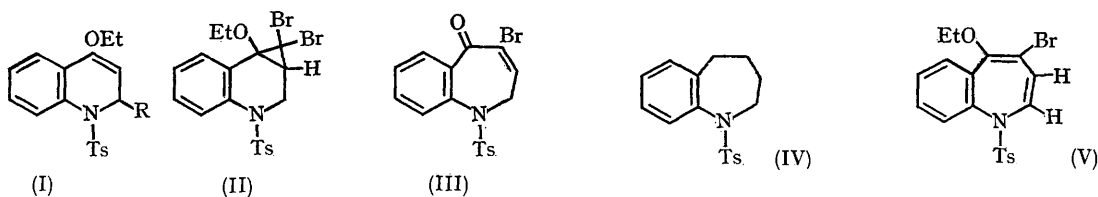
## A New Azepine and Azepinone Synthesis

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

NaOBu<sup>t</sup>)<sup>4</sup> yielded the dibromocyclopropane (II) (m.p. 131°) which reacted with silver nitrate in aqueous ethanol<sup>5</sup> to give, in 20% yield, a substance C<sub>17</sub>H<sub>14</sub>BrO<sub>3</sub>NS (m.p. 168°) which we regard



Ts = toluene-*p*-sulphonate

The enol-ether (I; R = H) (m.p. 87°)<sup>†</sup> and dibromo-carbene (from PhHgCBr<sub>3</sub><sup>3</sup> or CHBr<sub>3</sub> and

as (III). The latter ( $\nu_{\max}$  1665 cm.<sup>-1</sup>) has an n.m.r. spectrum consisting of a multiplet from  $\tau$ 2.05 to 3.0 (8 aryl and 1 olefin H), a doublet at

<sup>†</sup> Satisfactory analytical and mass spectrographic data were obtained for all new compounds.

$\tau$  5.4 ( $J$  5.5 c./sec., 2 methylene H), and a singlet at  $\tau$  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,<sup>4</sup> (II) gave in 35% yield a product (m.p. 98°) (C<sub>19</sub>H<sub>18</sub>BrO<sub>3</sub>NS) 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  $\tau$  2.2 to 2.95 (8 aryl H), a quartet at  $\tau$  3.8 ( $J$  7 c./sec., 2 olefin H), a blurred sextuplet at  $\tau$  6.8 (2 methylene H in nonequivalent magnetic

environment<sup>7</sup>), a singlet at  $\tau$  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.<sup>8</sup>

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