

BICYCLOBUTANES FROM 1,1-DIBROMO-2,2-DIALKYL-CYCLOPROPANES<sup>1,2</sup>

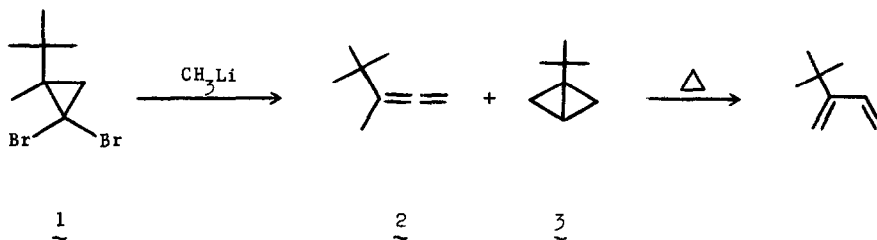
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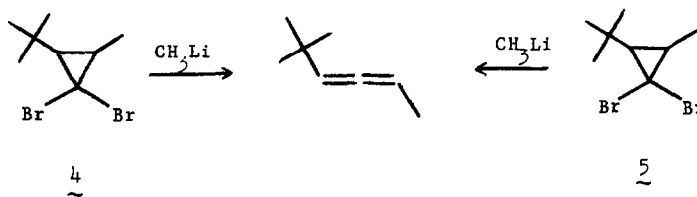
(Received in USA 23 May 1973; received in UK for publication 28 August 1973)

LaFLAMME and Doering<sup>4</sup> discovered the conversion of geminate-dibromocyclopropanes to allenes. Succeeding years have found numerous applications of the reaction in synthesis,<sup>5</sup> but relatively few investigations of the effects of simple alkyl substitution on the course of the reaction. A notable exception is the discovery, jointly by Skattebøl<sup>6</sup> and Moore and co-workers<sup>7</sup> that 1,1-dibromo-2,2,3,3-tetramethylcyclopropane gave not tetramethylallene but 1,2,2-trimethylbicyclo[1.1.0]butane on treatment with methyl lithium. This finding was expanded to cover other tetrasubstituted dibromocyclopropanes and mechanistic implications drawn,<sup>8,9</sup> but in non bicyclic systems tetrasubstituted species remained the sole precursors of bicyclobutanes. Indeed the contrast between tetrasubstitution, which gave bicyclobutanes, and trisubstitution, which gave allenes, has been often remarked.<sup>5,8,9</sup> We report here the formation of bicyclobutanes from sterically encumbered 2,2-disubstituted dibromocyclopropanes, with special emphasis on the 2-tert-butyl-2-methyl system.

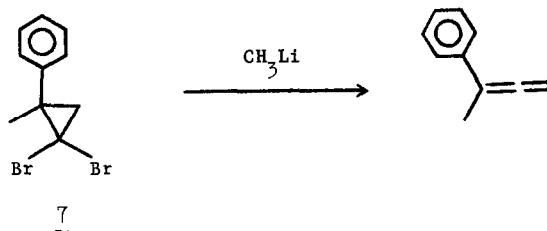
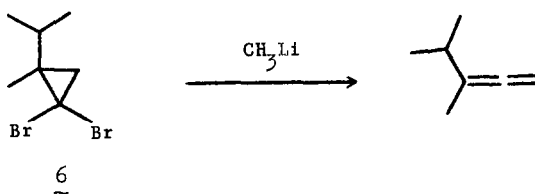
Treatment of 1,1-dibromo-2-tert-butyl-2-methylcyclopropane (1) with methyl lithium<sup>10</sup> at -50-30° resulted, after isolation and distillation, in a 70% yield of crude hydrocarbon. Gas-liquid-partition chromatography resolved two components, 1-tert-butyl-1-methylallene (2) and 1-tert-butylbicyclo[1.1.0]butane (3) in the ratio 3/2.<sup>11</sup> The formation of 3 seemed most remarkable in the light of past experience and it was identified not only by spectral analysis (with emphasis on a comparison with the known<sup>12</sup> 1-trimethylsilylbicyclo[1.1.0]-butane), but also by thermal conversion to the known<sup>13</sup> 2-tert-butylbutadiene.



There is a requirement for geminate substitution in the tert-butyl-methyl system, as neither cis- nor trans-1,1-dibromo-2-tert-butyl-3-methylcyclopropane (4,5) gave any detectable bicyclobutane.<sup>14</sup> Similarly, the steric bulk of the tert-butyl group is necessary,

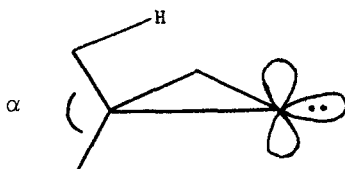


as 1,1-dibromo-2-isopropyl-2-methylcyclopropane (6) and 1,1-dibromo-2-phenyl-2-methylcyclopropane (7) gave only allene on treatment with methyllithium.



Presumably, other sterically crowded dialkyl dibromides should also give bicyclobutanes. Preliminary results with the neopentyl-methyl and isopropyl-ethyl systems reveal 10-20% bicyclobutanes. The 1,1-diethyl compound gave only allene.

The origin of the geminate dialkyl effect is not apparent in previous mechanistic discussions.<sup>9</sup> At this point we can only offer the tentative suggestion that the two alkyl groups may require an opening of the angle  $\alpha$ , forcing a carbon-hydrogen bond into better orientation for reaction with the empty p orbital, the presumed locus of initiation of the carbon-hydrogen insertion reaction.<sup>15,16</sup>



## REFERENCES AND NOTES

1. We thank the National Science Foundation for generous financial support through Grant GP-30797X.
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