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## Organic Preparations and Procedures International

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t902189982>

### AN IMPROVED SYNTHESIS OF METHYLENECYCLOPROPANE

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**To cite this Article** Krull, I. S. and Arnold, D. R.(1969) 'AN IMPROVED SYNTHESIS OF METHYLENECYCLOPROPANE', *Organic Preparations and Procedures International*, 1: 4, 283 – 285

**To link to this Article:** DOI: 10.1080/00304946909458400

**URL:** <http://dx.doi.org/10.1080/00304946909458400>

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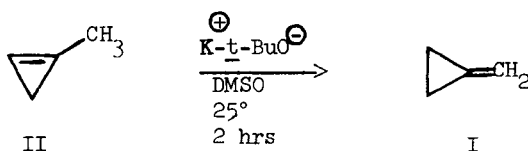
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## AN IMPROVED SYNTHESIS OF METHYLENECYCLOPROPANE

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All of the reported methods<sup>2-5</sup> for the preparation of methylenecyclopropane (I) have serious disadvantages, in particular the formation of mixtures, along with a low overall yield. The base-catalyzed isomerization of 1-methylcyclopropene<sup>6-8</sup> appeared to be a promising route for preparation of I.<sup>9</sup>



1-Methylcyclopropene (II)<sup>11</sup> was treated with a catalytic amount of potassium t-butoxide in DMSO for 2 hrs at room temperature. A quantitative yield of the desired methylenecyclopropane was obtained. This was identified by its characteristic nmr, ir and mass spectra.<sup>2,12</sup> Some methylenecyclopropane (10%) was also formed during the synthesis of 1-methylcyclopropene, but was apparently not detected in the original report.<sup>11</sup>

Experimental

Methylenecyclopropane (I). 1-Methylcyclopropene (II) was prepared and purified as described previously in 50-60% yield.<sup>11</sup> The cyclopropene II

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(1.0 g) was transferred on a high-vacuum line to a trap containing anhydrous potassium t-butoxide (K and K Labs, 100 mg) in 5 ml of dimethyl sulfoxide (which was distilled from calcium hydride). The solution was warmed to room temperature, and kept there for 2-3 hours. Transfer of the gaseous material to another vacuum trap maintained at 77°K, gave pure (> 99%) methylene-cyclopropane (0.95 g, 95% yield). Nmr spectrum (CDCl<sub>3</sub>): δ 5.4 (quintuplet, J=2.1 Hz, 2H); δ 1.05 (triplet, J=2.1 Hz, 4H).<sup>12</sup> The ir spectrum agreed precisely with that reported,<sup>2</sup> and the mass spectrum showed m/e = 54 (parent), 53, 39 (base), 28, 27 and 26.<sup>13</sup> Vpc analysis on a Porapak S column (6' x 1/4") at 85° (flow = 50 ml/min) showed only a single compound (retention time = 12.5 mins). The overall yield of I starting from commercially available materials was > 50%.

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9. Since the completion of this work, the reaction of methallyl chloride with potassium amide has been reported to afford methylenecyclopropane in 36% yield and 97% purity.<sup>10</sup>
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13. We wish to thank Dr. P. O. Schissel and Mr. P. F. D'Angelo for the mass spectral results.

(Received July 25, 1969)