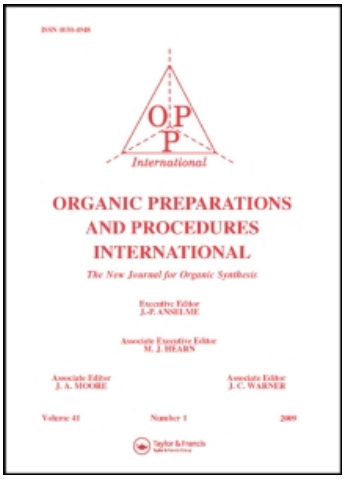

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AN IMPROVED SYNTHESIS OF METHYLENECYCLOPROPANE

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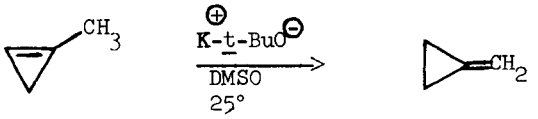
All of the reported methods[2-5] for the preparation of methylenecyclopropane (I) have serious disadvantages, in particular the formation of mixtures, along with a low overall yield. The base-catalyzed isomerization of 1-methylcyclopropene[6-8] appeared to be a promising route for preparation of I.[9]



II I

1-Methylcyclopropene (II)[11] 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.[2,12] Some methylenecyclopropane (10%) was also formed during the synthesis of 1-methylcyclopropene, but was apparently not detected in the original report.[11]

Experimental

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

(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%) methylenecyclopropane (0.95 g, 95% yield). Nmr spectrum ($CDCl_3$): δ 5.4 (quintuplet, J=2.1 Hz, 2H); δ 1.05 (triplet, J=2.1 Hz, 4H).[12] The ir spectrum agreed precisely with that reported,[2] and the mass spectrum showed m/e = 54 (parent), 53, 39 (base), 28, 27 and 26.[13] 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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