

SYNTHESIS AND PROOF OF STRUCTURE OF ISOPROPENYLIDENECYCLOPENTANE:  
GENERATION OF 1-ISOBUTENYL-CYCLOPENTENE VIA TWO INDEPENDENT ROUTES

R. B. Reinartz\* and G. J. Fonken

Department of Chemistry, The University of Texas at Austin

Austin, Texas 78712

(Received in USA 13 August 1973; received in UK for publication 5 October 1973)

Synthesis of 1,1-dibromo-2,2-dimethylspiro[2.4]heptane (1) was accomplished by dibromocarbene addition to isopropylidenecyclopentane<sup>1,2,3</sup>. Since tetraalkyl-substituted *gem*-dibromocyclopropanes with methyl lithium usually yield exclusively bicyclobutanes<sup>4,5,6</sup>, 1 was reacted with methyl lithium. Although bicyclobutane 2 was the expected product, a 60% yield of isopropenylidenecyclopentane (3) was obtained. Identification of 3 was by spectral data [ $\text{NMR}$  1.60  $\delta$  (singlet, 6H), 2.40  $\delta$ -2.10  $\delta$  (multiplet, 4H), 1.80  $\delta$ -1.45  $\delta$  (multiplet, 4H); IR 1960  $\text{cm}^{-1}$  (weak), 1400  $\text{cm}^{-1}$ , 1372  $\text{cm}^{-1}$ , 1362  $\text{cm}^{-1}$ , 1042  $\text{cm}^{-1}$ , 945  $\text{cm}^{-1}$ ; mass spectrum with parent peak at 122] and a suitable elemental analysis. The band at 1960  $\text{cm}^{-1}$  observed in the IR indicative of an allene was small. However, the bulk of the evidence suggested the allene identity. Therefore, to confirm the structure, an authentic sample of allene 3 was prepared via the method of Rona and Crabbe<sup>7</sup> using lithium dimethyl copper reagent on acetate 4. All spectral data from the compounds prepared in both sequences were identical, demonstrating that 3 was produced in the methyl lithium reaction on 1. It should be noted that this allene was present both before and after VPC purification on a 5 ft x 1/4 in aluminum column packed with 60/80 mesh chromosorb G, 2% KOH, and 20% squalene which was used for all separations.

The occurrence of allene 3 is significant since other investigators have demonstrated only bicyclobutanes produced from comparable systems. For example, Moore *et al.*<sup>4,5</sup> reported bicyclobutanes from reaction of methyl lithium on 1,1-dibromo-2,2,3,3-tetramethylcyclopropane, 1,1-dibromo-2,2-diethyl-3,3-dimethylcyclopropane, and 1,1-dibromo-2,2,3,3-tetraethylcyclopropane. Skattebol<sup>6</sup> and Reinartz<sup>8</sup> reported bicyclobutane formation from the first of these tetraalkyl-substituted precursors. Also, the homolog of 1, 1,1-dibromo-2,2-dimethylspiro[2.5]octane, was

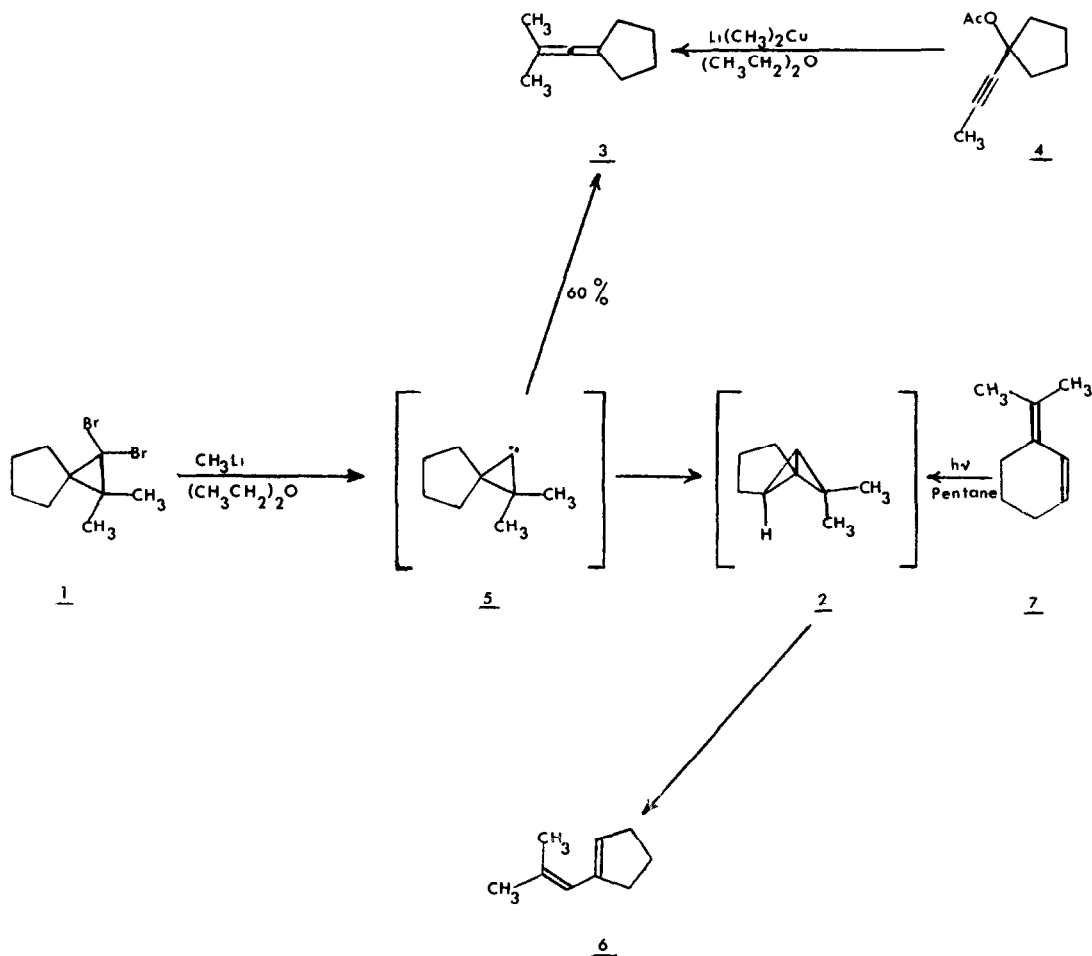
shown to yield only bicyclobutanes<sup>8</sup>. The occurrence of 2 from the methyl lithium reaction reported here probably is explained by the slower rate of insertion of the intermediate cyclopropylidene 5 in relation to allene production.

The second product (30%) from the methyl lithium reaction of 1 was identified as 1-isobutenylcyclopentene (6), by comparison to an authentic sample<sup>9</sup>, which presumably arose from the isomerization of 2 during attempted VPC purification. All attempts to purify 2 without rearrangement were futile, although it was established by NMR and IR data that 2 was probably present and not diene 6 in the freshly quenched reaction mixture. The isolation of diene 6 was not surprising and demonstrated that a bicyclobutane had very likely been present. The catalysis of bicyclobutanes by Lewis acids has been shown to yield dienes<sup>6,9,10,11,12,13</sup>. Since the column packing contains materials which can act as Lewis acids, the purification itself likely resulted in rearrangement to the diene. Other isolation procedures utilizing numerous packing substances also were futile.

The methyl lithium reaction on the tosylhydrazone of 2-isopropylidenecyclohexanone<sup>14</sup> produced 3-isopropylidenecyclohex-1-ene (7)<sup>8</sup>. The identification of 7 was based on spectral data [ $\text{NMR } 6.27 \delta$  (doublet of triplets,  $J=10$  hz,  $J=1.5$  hz, 1H),  $5.48 \delta$  (doublet of triplets,  $J=10$  hz,  $J=4$  hz, 1H),  $2.35 \delta$ - $1.75 \delta$  (multiplet, 6H),  $1.63 \delta$  (singlet, 6H); IR  $3010 \text{ cm}^{-1}$ ,  $1630 \text{ cm}^{-1}$ ,  $1600 \text{ cm}^{-1}$ ,  $1370 \text{ cm}^{-1}$ ,  $1250 \text{ cm}^{-1}$ ,  $724 \text{ cm}^{-1}$ ; mass spectrum with parent peak at 122; UV with  $\lambda_{\text{max}}=236 \text{ nm}$  and  $\epsilon_{\text{max}}=18,500$ ] and a suitable elemental analysis. This *s-trans* diene was chosen for photolysis in an effort to generate the bicyclobutane 2 since, based on previous work<sup>8,9,15,16</sup>, photolytic closure to this bicyclobutane was anticipated. Evidence from the photolysis of 7 suggested a bicyclobutane which could not be isolated and instead rearranged during chromatographic separation to only 6. The methyl lithium reaction on 1 and the photolysis of 7 likely shared a product in common, logically the expected bicyclobutane 2, as is suggested by the rearrangement diene 6. It should be noted that 7, on photolysis, via a mechanism resembling di- $\text{TF}$ -methane rearrangements, might result in 6-isopropylidenebicyclo[ $\overline{3.1.0}$ ]hexane which could isomerize to diene 6. However, a methyl homolog of 7, on photolysis, yielded a bicyclobutane and when subjected to similar VPC conditions led to a methyl homolog of 6<sup>9</sup>. Because of compound similarity, this data supports the existence of bicyclobutane 2 in the photolysis of 7.

In conclusion, it has been shown for the first time that methyl lithium reaction of 1, a tetraalkyl-substituted *gem*-dibromocyclopropane, produced a 60% yield of allene 3 which was confirmed by an authentic sample. In essence, allene formation is preferred in this case over

insertion of the cyclopropylidene to give bicyclobutane 2. Efforts to prepare the expected bicyclobutane without rearrangement via a photolysis on *s-trans* diene 7 were also disconcerting in that diene 6 again was obtained by rearrangement. Preparation and purification of bicyclobutanes of strain on the order of that exhibited in 2 is feasible if separation can be achieved without rearrangement. Evidence indicates that if two of the alkyl groups of a tetraalkyl-substituted *gem*-dibromocyclopropane are part of a ring, on reaction with methyl lithium, bicyclobutane formation is expected if the compound is not too strained<sup>8</sup>; however, if the ring size is decreased to five carbons, a predominance of allene is obtained.



**Acknowledgement.** The authors are grateful to the Robert A. Welch Foundation for predoctoral and research grant support.

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\*Author to whom correspondence should be addressed at Department of Chemistry, North Texas State University, Denton, Texas 76203

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