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GENERATION OF CYCLOPROPYLIDENES FROM GEM-DIHALOPROPANES UNDER ULTRASONIC IRRADIATION

Linxiao Xu Fenggang Tao Tongyin Yu*

Institute of Material Science, Fudan University, Shanghai, China

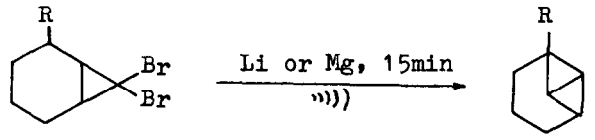
ABSTRACT: Cyclopropylidenes can be generated much quickly by reactions of gem-dihalocyclopropanes and metals (Li, Na or Mg) under ultrasonic irradiation. The reactions usually complete in 5-15min at room temperature.

Recently, it was found that many heterogeneous organic reactions could be promoted by ultrasonic irradiation. Some of the successful applications in this field are preparations of organometallic reagents from the reactions of alkyl or aryl halides with metals, such as lithium, magnesium and zinc et al.[1-5] Now, we would like to report a modified method for the generation of cyclopropylidenes from the reactions of gem-dihalocyclopropanes with lithium, sodium or magnesium under ultrasonic irradiation.

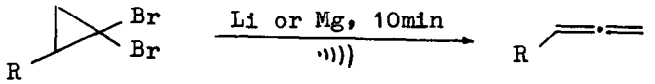
It is well known that gem-dihalocyclopropanes, particularly gem-dibromocyclopropanes, on reacting with sodium, magnesium or alkyl lithium are dehalogenated to form the corresponding carbenoids, subsequently to cyclopropylidenes, which can rearrange into allenes or insert into the adjecent C-H bond.[6-9] When using alkyl lithium instead, besides alkyl halide formed by Li-halo exchange, the reaction frequently gives alkylated by-products, often making the separation and purification difficult.

Under the influence of ultrasound, the cyclopropylidenes can be generated without induction period by the reactions of gem-dihalocyclopropanes and lithium,

sodium or magnesium in anhydrous THF under nitrogen. Most of the reactions usually complete in 5-15 minutes at room temperature. For gem-dibromocyclopropanes, the use of lithium wire or magnesium turnings in the reactions give similar results. The intramolecular C-H bond inserted products or allenes can be obtained in 10-15 minutes. The solvent used is important in which THF is better than others. If n-pentane is used as the solvent instead of THF, the rate of reaction slows down enormously.



(R= H, Me)

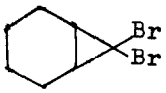
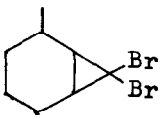
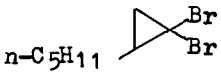
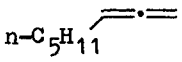
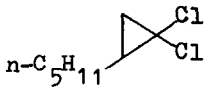
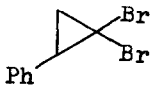
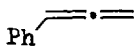
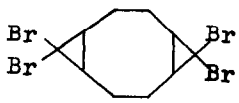
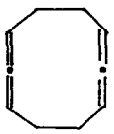


(R= $n\text{-}C_5H_{11}$, Ph)

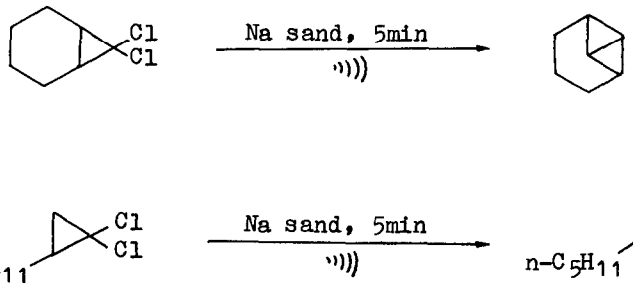
The above reactions can also be carried out without nitrogen protection and in commercial THF dried over KOH. But in this way, the reactions accompany an induction period over 5-10 minutes.

Unlike gem-dibromocyclopropanes, gem-dichlorocyclopropanes are more difficult to react with lithium or magnesium. No cyclopropylidene was generated when 7,7-dichlorobicyclo[4.1.0]heptane was reacted with magnesium turnings even refluxing in THF. And when it did react with lithium wire, longer reaction time was necessary (over 5 hours). In the previous paper,[10] we dispersed sodium on the surface of alumina, the corresponding cyclopropylidene was generated by the reaction of gem-dichlorocyclopropane and sodium with high surface. Under ultrasonic irradiation, better results were obtained by using sodium wire instead of lithium wire and the reaction time could be shortened to 2 hours. If sodium sand freshly prepared in xylene under ultrasonic irradiation, the reaction time could be further cut short to only 5 minutes. The results obtained were similar to that of gem-dibromocyclopropanes and lithium or magnesium.

TABLE Results of the Reaction of gem-Dihalocyclopropanes and Metals under Ultrasonic Irradiation[a]

gem-Dihalocyclopropane	Metal	Main Product[b]	Irradiation Time (min)	Isolated Yield (%)
	Li		15	46
	Mg		15	44
	Na		5	30
	Li		15	52
	Mg		10	55
	Li		10	81
	Mg		10	87
	Na		5	68
	Mg		10	76
	Li		20	63

(a) Room temperature; (b) Identified by ^{1}H NMR, IR and GC-MS, the spectra obtained were the same as that in literature.



The typical experimental procedure is as follows: To 0.05 mol of lithium wire (0.5-1 cm segments) or magnesium turnings or sodium sand in 20 ml of anhydrous THF, 0.02 mol of gem-dihalocyclopropane was added. The mixture was placed in an ultrasound laboratory cleaner, immersed to the solvent level (the water temperature was 20 °C). After 5-15 minutes of ultrasonic irradiation, the excess metal was removed by filtration, and 25 ml of water were added to the filtrate. It was extracted with n-pentane, dried over $MgSO_4$ and distilled, (see the table).

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