Cyclobutylidenes from Geminal Dihalogenocyclobutanes[1]

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Cyclobutylidene, or a related carbenoid, can be generated by reaction of geminal dibromocyclobutane with methyl-lithium at temperatures as low as −78 °C to yield methylenecyclopropane and cyclobutene nearly quantitatively.

The base-induced thermal decomposition of cyclobutanone tosylhydrazones (Bamford–Stevens reaction) at temperatures generally above 150 °C is the nearly-exclusively applied method for the generation of cyclobutylidenes.[2] Typical reactions of cyclobutylidene (**1**) generated from (**2**) are ring-contraction to methylenecyclopropane (**3**) (80%) and 1,2-hydrogen-shift to give cyclobutene (**4**) (20%) (Scheme 1).[3]

Cyclopropylidenes (**5**),[4] on the contrary, are usually generated from readily available geminal dihalogenocyclopropanes by reaction with alkyl-lithium at temperatures below 25 °C. Halogen–metal-exchange to 1-lithio-1-halogenocyclopropanes, followed by α-elimination of the lithium halide, gives (**5**) or related carbenoids (Scheme 1). The corresponding organometallic route to cyclobutylidenes (carbenoids), however, is unknown. We report on the reaction of geminal dihalogenocyclobutanes with alkyl-lithium.

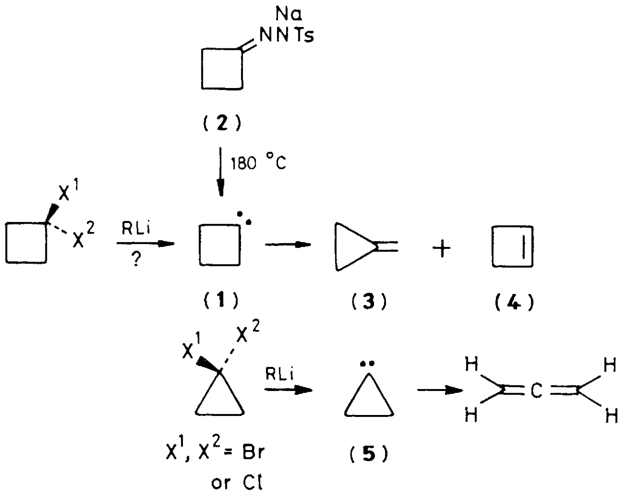
Only 1,1-dichlorocyclobutane (**6**) is directly available by reaction of cyclobutanone (diethyl ether, 35 °C) with PCl_5.[5] Compounds (**7**)—(**10**) are prepared by HX-addition (X = Cl, Br,[6,7] I) to 1-bromocyclobutene (**11**),[8] compound (**11**) being previously obtained in good yield from cyclobutene[9,10] by addition of bromine[10,6] and subsequent elimination of HBr[8] (Scheme 2).

Geminal dihalogenocyclobutanes were allowed to react with alkyl-lithium for 30 min either in solution (−78 up to 0 °C) or in a tube packed with alkyl-lithium-coated glass chips[11] at

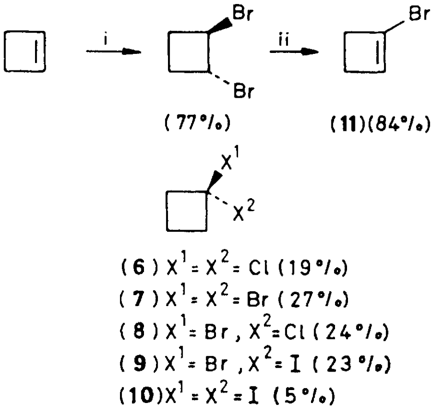
Table 1. Reactions of (6)—(9) with alkyl-lithium, RLi.[a]

Entry no.	Technique[b]	Compound	Solvent	T/°C	Additional conditions[c]	R	Total yield (%) (3) + (4)[d]	Ratio (3):(4)
1	(A)	**(6)**	Et_2O	0		Me	0	
2	(A)	**(6)**	Et_2O	0		Bu^n	3–4	4.65
3	(A)	**(7)**	Et_2O	0 to −78		Me	90–100	5.93
4	(A)	**(7)**	THF	0		Me	100	3.51
5	(A)	**(7)**	Et_2O	0	0.5 equiv. 12-crown-4	Me	89	5.30
6	(A)	**(7)**	Et_2O	0	1.0 equiv. 12-crown-4	Me	84	3.20
7	(A)	**(7)**	Et_2O	0	4.0 equiv. 12-crown-4	Me	93	1.71
8	(A)	**(7)**	Et_2O	0	1.0 equiv. TMEDA	Me	35	4.44
9	(A)	**(8)**	Et_2O	0		Me	76	5.40
10	(A)	**(9)**	Et_2O	0		Me	96	5.96
11	(B)	**(6)**		20	10^{-3} Torr	Me	0.1	2.07
12	(B)	**(6)**		20	10^{-3} Torr	Bu^n	1.7	2.60
13	(B)	**(7)**		20—100	10^{-3} Torr	Me	67	2.00
14	(B)	**(9)**		20	10^{-3} Torr	Me	81	1.90

[a] Standard conditions: time of reaction = 30 min; molar excess of RLi = 1.07 [for technique (A)]. [b] (A) = RLi/solvent, (B) = 'RLi-tube.' [c] The equivalents of 12-crown-4 and TMEDA added refer to MeLi. [d] Determined by v.p.c. with but-2-yne as internal standard.



Scheme 1. Ts = tosyl.



Scheme 2. i, Br_2, $CHCl_3$, −10 °C (ref. 10); ii, KOH (powder), 110 °C. Yields (in parentheses) are not optimized.

temperatures between 20 and 100 °C. When both methods were applied to the reaction of 1,1-dichlorocyclobutane (**6**) with methyl-lithium no methylenecyclopropane (**3**) or cyclobutene (**4**) could be detected; if butyl-lithium was used, (**3**) and (**4**) were formed in yields up to 4% (Table 1). However, the geminal dibromide (**7**) on reaction with methyl-lithium in diethyl ether at temperatures ranging from −78 up to 0 °C gave nearly quantitatively, (**3**) and (**4**)† in a ratio which was slightly greater than that obtained from the Bamford–Stevens reaction of (**2**). A tenfold excess of methyl-lithium did not affect yield or ratio of (**3**) and (**4**), but a distinctly smaller ratio was observed with the 'MeLi-tube' technique[11] which afforded less hydrocarbons (67%) but which also gave bromocyclobutane (9%) and 1-bromocyclobutene (**11**) (2%), as byproducts. Between 20 and 100 °C the product distribution proved to be independent of temperature,[11] (entry 13, Table 1). Bromocyclobutane and 1-bromocyclobutene (**11**) could not be detected in the reaction of (**7**) with MeLi in solution.

Good-to-excellent yields and similar product ratios to those for the reaction of (**7**) with methyl-lithium in diethyl ether were obtained with the mixed geminal dihalogenocyclobutanes (**8**) and (**9**). If the reaction of (**7**) was performed in tetrahydrofuran (THF) the hydrocarbons (**3**) and (**4**) were obtained in the same yield, but in a different ratio. The yield of (**3**) and (**4**) for the reaction of (**7**) with methyl-lithium in diethyl ether in the presence of different molar amounts of 12-crown-4 ether was unchanged, but the ratio decreased with increasing amounts of crown-ether added (entries 5—7). Finally, when (**7**) was allowed to react with methyl-lithium in the presence of tetramethylethylenediamine (TMEDA), it was largely unchanged and only 35% of (**3**) and (**4**) was formed. For the Bamford–Stevens reaction of (**2**) no absolute yields of the hydrocarbons produced have been reported in the literature.[3] Flash-pyrolysis of (**2**) under our conditions (180 °C/10^{-3} Torr) confirmed the ratios of (**3**) (81.1%), (**4**) (17.1%), and buta-1,3-diene (1.8%) found earlier. However, the total yield (32%) was substantially lower compared with the reactions of (**7**), (**8**), and (**9**) with methyl-lithium.

In conclusion, we have shown that dihalogenocyclobutanes, in which at least one halogen is bromine or iodine, on reaction with methyl-lithium in diethyl ether at temperatures ≤0 °C, give methylenecyclopropane (**3**) and cyclobutene (**4**) in high yields in a slightly larger ratio than is found in the pyrolysis of cyclobutanone tosylhydrazone sodium salt (**2**). This suggests that in both reactions similar reactive intermediates *i.e.* cyclobutylidenes are operative.

From a synthetic point of view this preparation of dihalogenocyclobutanes seems to be more laborious than the formation of tosylhydrazones from ketones. However,

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† For v.p.c.-analysis with but-2-yne as internal standard, (**3**) and (**4**) were pumped off after reaction into a trap.

whereas the Bamford–Stevens reaction requires high temperatures, the generation of cyclobutylidenes *via* the organometallic route may be carried out at low temperatures, making the latter method especially appropriate where thermally labile products are expected.

We thank Deutsche Forschungsgemeinschaft for financial support of this work.

Received, 2nd March 1982; Com. 233

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