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ALLENES FROM *gem*-DIHALOCYCLOPROPANE DERIVATIVES AND ALKYLLITHIUM

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IN a recent communication [1] Moore and Ward describe the preparation of allenes from *gem*-dibromocyclopropanes and alkyllithium. We wish to report some additional results, particularly the preparation of two cyclic diallenes, which further establish the generality of this reaction.

gem-Dibromocyclopropanes gave allenes in good yields when treated with methyl- or buthyllithium in ether. The dichloro analogues also reacted readily with butyl-lithium, but we have not been able to observe any reaction with methyllithium. Table I gives some of the results obtained.

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[1] W.R. Moore and H.R. Ward, *J. Org. Chem.* **25**, 2073 (1960).

TABLE I

The reaction between 1, 1-dihalocyclopropanes and alkyllithium.

gem-Dibromocyclopropane derivative of	alkyl-lithium	allene	yield %
Trimethylethylene	MeLi	2-methylpenta-2, 3 diene	69 [a]
"	BuLi		68
Tetramethylethylene	MeLi	2, 4-dimethyl-penta-2, 3-diene	73 [a]
"	BuLi	"	69
Hexa-1, 5-diene	MeLi	hepta-1, 2, 6-triene	72 [b]
1, 1-Diphenylethylene	MeLi	1, 1-diphenylpropa-1, 2-diene	43 [c]
Styrene	MeLi	1-phenylpropa-1, 2 diene	82 [a]
Cyclooctene	MeLi	cyclonona-1, 2-diene	93 [d]
Cycloocta-1, 5-diene	MeLi	cyclonona-1, 2, 6-triene	76 [e]

[a] b. p. and refractive index were identical with those of the literature.
[b] b. p. 102°, n_D^{24} 1.4551, (Found:C, 88.93 ; H, 10.78 %). [c] b. p. 75-76°/0.01 mm, n_D^{20} 1.6313 (Found : C, 92.88 ; H, 6.23 %). The compound polymerized during the distillation. [d] b. p. 62°/16 mm, n_D^{20} 1.5060 (Found : C, 88.43 ; H, 11.44 %). [e] b. p. 61°/13 mm, n_D^{24} 1.5216 (Found : C, 89.60 ; H, 9.84 %).

All the *gem*-dihalo cyclopropane derivatives were prepared from the olefins and dibromocarbene essentially as described by Doering and Hoffmann.[2] The halide was dissolved in dry ether, and the ethereal alkyllithium was added dropwise with stirring usually at -30 to -40°. The allenes were characterized by their boiling points, refractive indices and analyses. The infrared spectra supported the identity of

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[2] W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.* **76**, 6162 (1954).

the products and further showed to what extent an allene-acetylene rearrangement had taken place. This was rare when methyllithium was used ; with butyllithium, however, a certain amount of rearrangement occurred probably because of the unavoidable presence of alkoxides in this reagent. Another disadvantage encountered using butyllithium was the separation of the allenic product from the butyl halide formed in the reaction. Thus, 1, 1-dichloro-2,2,3- trimethylcyclopropane with butyllithium yielded 2-methylpenta-2, 3-diene, as indicated by the infrared spectrum, but a separation from butyl chloride was not achieved. Generally the best results were obtained using the gem-dibromocyclopropanes and methyllithium.

Cycloocta-1,5-diene gave with dibromo-carbene besides the monoadduct also 34% of 9,9,10,10-tetrabromotricyclo $[7,1,0,0^{1,8}]$ decane (I), m.p. 174-180° (Found : C, 26.69 ; H, 2.62 %). In the same way cyclotetradeca-1,9-diene gave 22% of 15, 15, 16, 16-tetrabromotricyclo $[13, 1, 0, 0^{1,14}]$ hexadecane (II), m.p. 200-204° (Found : C, 35.68 ; H, 4.38 %). When (I) was treated with methyllithium at -40° a small amount of cyclodeca- 1,2,6,7-tetraene (III) was obtained, m.p. 36° (Found : C, 90.74 ; H, 9.31 %). The infrared spectrum shows strong bands at 1960 and 856 cm^{-1} characteristic of the allene grouping.[3] No acetylenic absorption was

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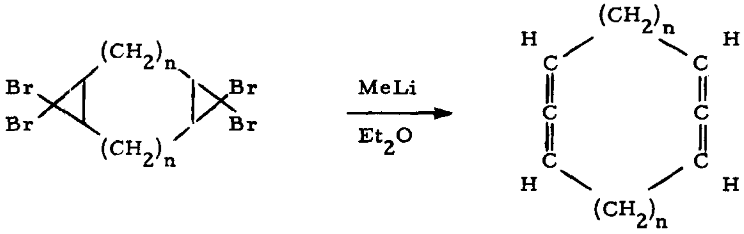
[3] J. H. Wotiz and D. E. Mancuso, J. Org. Chem. 22. 207 (1957).

present. The ultraviolet spectrum shows only end-absorption down to 200 mμ. Similarly (II) yielded 52 % of cyclohexadeca-1,2,9,10-tetraene (IV), m.p. 80° (Found : C, 88.75 ; H, 11.13 %). The infrared spectrum shows strong bands at 1970 and 894 cm^{-1} and no acetylenic absorption. In the ultraviolet region only end-absorption is observed. The structure of these cyclic diallenes was further established by ozonolysis and subsequent oxidation by peracetic acid [4] to the expected dicarboxylic acids.



I (n = 2)

II (n = 5)

III (n = 2)

IV (n = 5)

We have not been able to obtain any allenic products from the reactions of 7,7-dibromobicyclo[4,1,0] heptane or 8,8-dibromobicyclo[5,1,0] octane with methyllithium at -70°. In the former case the main products were a low boiling olefin and a high boiling oxygen-containing liquid.

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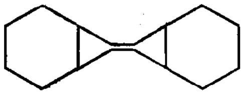
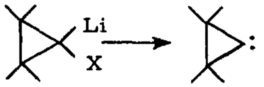
[4] Wilms, *Ann.* **567**, 96 (1950).

From the residue a small amount of a crystalline compound was obtained which after recrystallization and sublimation melted at 124°C (Found : C, 89.17 ; H, 10.73 % ; mol. wt.[5] 188), U.V. λ_{max} (n-hexane ; 1 mm cell) 198 mμ (ε ~ 15000) and 206 mμ (shoulder ; ε ~ 13500). The infrared spectrum (KBr disc) has a band at 2985 cm^{-1}[6], and no bands indicating olefinic bonds. The N.M.R. spectrum[7] at 60 M.C. in deuterated benzene shows three bands at τ = 8.20, 8.30 & 8.68 relative to tetramethylsilane as internal standard and the absence of olefinic protons. There is little doubt that this compound is identical with that, m.p. 120.5 - 121°C, isolated by Moore and Ward[1], who assigned the structure (V).



V



(X = Cl or Br) VI

An attempt to demonstrate the existence of the carbene intermediate (VI), suggested[8] for a related reaction, by using any of the gem-dihalocyclopropane derivatives and isobutylene, tetramethylethylene or triphenylphosphine as acceptors failed.

Miller and Kim[9] have generated dihalocarbenes by treatment

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[5] We thank Dr. J. Block for the mass-spectrometric determination.

[6] This could be the cyclopropane C-H stretching vibration.

[7] Kindly carried out by Dr. J.F.M. Oth.

[8] W. von E. Doering and P.M. La Flamme, Tetrahedron 2, 75 (1958).

[9] W.T. Miller and C.S.Y. Kim, J. Am. Chem. Soc. 81, 5008 (1959).

of carbon tetrahalides with alkyllithium. When we reacted an equimolar mixture of carbon tetrabromide and trimethylethylene with an excess of methyllithium (> 2 moles per mole CBr_4), 50 % yield of 2-methylpenta-2,3-diene was obtained. This result may also explain the low yield of dibromonorcarane (11 %) obtained by the above authors from a reaction of carbon tetrabromide and butyllithium in the presence of cyclohexene.

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