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STUDY ON THE INFLUENCE OF UNSATURATIONS ON THE FORMATION OF C-11, C-12, C-13 AND C-14 MEMBERED RINGS

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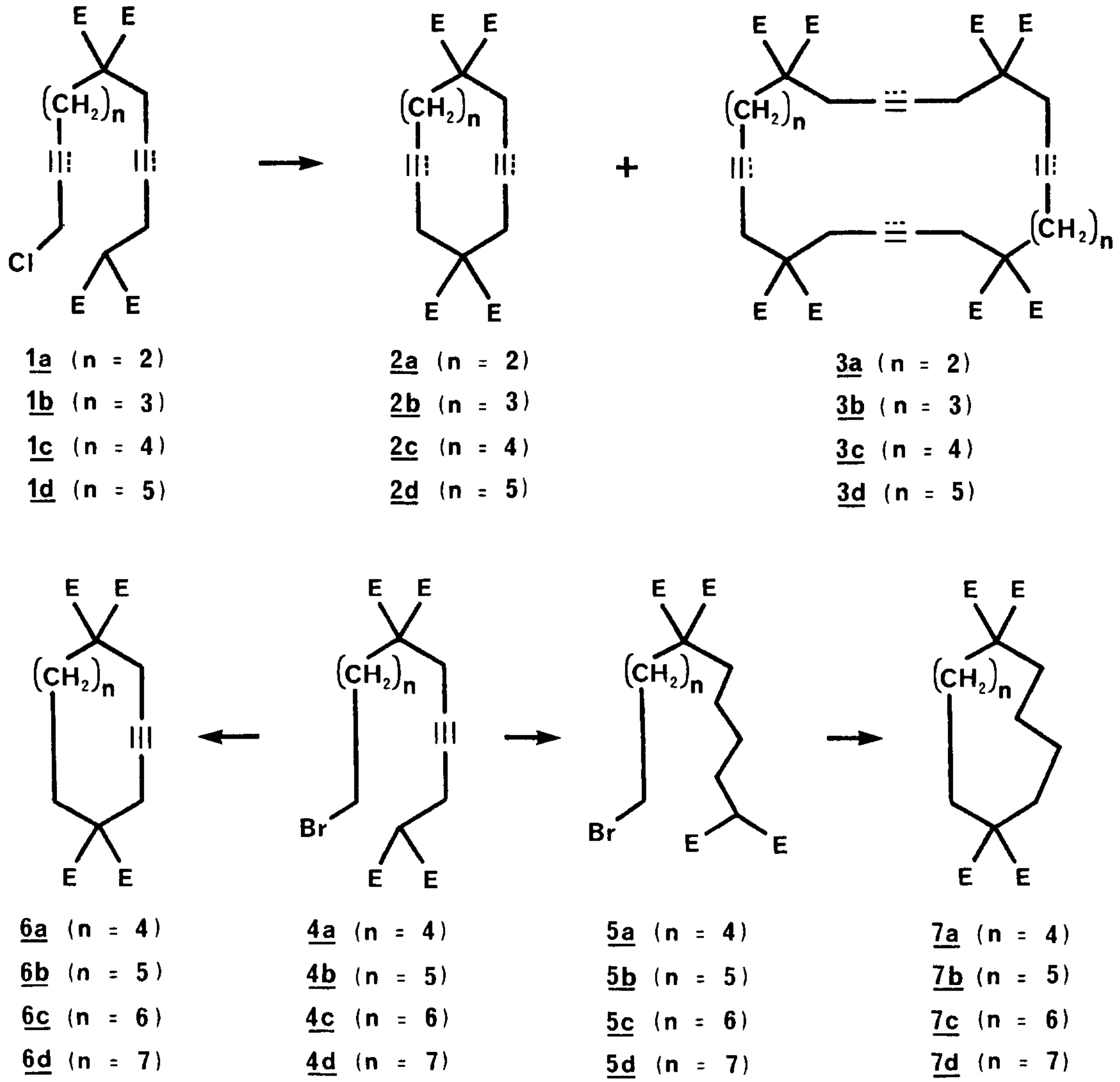
Abstract. The intramolecular displacement of allylic and propargylic chlorides and primary bromides by malonate anion in eleven, twelve, thirteen and fourteen carbon chains containing either two, one or no unsaturation, is reported. At 2×10^{-2} M, formation of cyclic monomers and dimers are observed in all cases. At 2×10^{-3} M, the cyclic monomer is the predominant product which is formed in good yield in most cases.

Studies on medium and large carbocyclic rings containing various functional groups and substituents is an important area of research which has not yet been explored in detail.[1] One of the reasons is the lack of reliable direct synthetic methods. We have recently reported[2] that 10-membered ring can be obtained in good yield by a direct cyclization method at medium dilution, provided that the aliphatic chain contains two unsaturation centers (cis and trans double bond or triple bond). As a continuation of this study, we wish to report a similar investigation on the cyclization of C-11, C-12, C-13 and C-14 carbon chains.

Cyclization of the C-11, C-12, C-13 and C-14 aliphatic chains 1a-d[3] (Scheme 1) can either yield besides polymerization, the corresponding cyclic monomer (2a-d) and/or dimer (3a-d). The two unsaturations in the chain are either a cis (C) or a trans (T) olefin or an acetylene (A). The following combinations were studied: 1a-d -[C-C], -[C-T], -[T-T], -[A-C], -[A-T] and -[A-A]. The cyclization of C-11, C-12, C-13 and C-14 aliphatic chains 4a-d[3] and 5a-d[3] having respectively only one unsaturation (an acetylene) and no unsaturation was also investigated. These compounds can also give besides polymerization, their corresponding cyclic monomers (6a-d and 7a-d) and/or dimers (structures not shown).



[E = $COOCH_3$]

SCHEME 1

The cyclization reactions were carried out in the presence of potassium carbonate in a 1:1 mixture of tetrahydrofuran and N,N-dimethylformamide at 90°C. The reactions were performed at a concentration of 2 x 10^{-2} and 2 x 10^{-3} molar and the results are shown in Tables 1 and 2 respectively. The cyclic monomers[4] and dimers[4] were readily separated by chromatography. They are all crystalline with the exception of two monomers (2a-[T-T] and 2d-[C-C]). At 2 x 10^{-2} M,

TABLE 1. **Yields[a] of cyclic monomer and dimer at 2 x 10^{-2} M**

	Length of chain			
	C-11	C-12	C-13	C-14
Unsaturations	M - D = T[b]	M - D = T	M - D = T	M - D = T
[C-C]	16 - 29 = 45	28 - 42 = 70	67 - 11 = 78	69 - 4 = 73
[C-T]	22 - 46 = 68	11 - 58 = 69	8 - 48 = 56	21 - 40 = 61
[T-T]	8 - 63 = 71	28 - 46 = 74	13 - 40 = 53	7 - 33 = 40
[A-C]	47 - 29 = 76	80 - 3 = 83	91 - 4 = 95	81 - 3 = 84
[A-T]	16 - 20 = 36	59 - 22 = 81	59 - 23 = 82	10 - 27 = 37
[A-A]	54 - 25 = 79	51 - 19 = 70	68 - 18 = 86	41 - 26 = 67
Mono [A]	—— [c]	——	——	——
Saturated	——	——	——	——

[a] Average value obtained from (two) chromatography.
[b] M = % monomer; D = % dimer; T = total of monomer + dimer.
[c] Not carried out.

TABLE 2. **Yields[a] of cyclic monomer and dimer at 2 x 10^{-3} M**

	Length of chain			
	C-11	C-12	C-13	C-14
Unsaturations	M - D = T[b]	M - D = T	M - D = T	M - D = T
[C-C]	52 - 12 = 64	61 - 15 = 76	77 - 3 = 80	76 - - = 76
[C-T]	66 - 15 = 81	38 - 33 = 71	20 - 23 = 43	52 - 19 = 71
[T-T]	32 - 37 = 69	63 - 14 = 77	45 - 21 = 66	20 - 17 = 37
[A-C]	85 - 8 = 93	90 - - = 90	95 - - = 95	85 - - = 85
[A-T]	44 - 7 = 51	86 - 5 = 91	83 - 4 = 87	41 - 19 = 60
[A-A]	87 - 8 = 95	79 - 4 = 83	89 - 3 = 92	76 - 7 = 83
Mono [A]	40 - 17 = 57	39 - 16 = 55	53 - 14 = 67	55 - 16 = 71
Saturated	2 - 2 = 4	29 - 6 = 35	44 - - = 44	52 - 4 = 56

[a] Average values obtained from (two) chromatography.
[b] M = % monomer; D = % dimer; T = total of monomer + dimer.

the sum of monomer and dimer is important in all cases and cyclization to yield the large ring dimer is a process which can easiliy compete with polymerization. The results in Table 1 also indicate that the presence of a triple bond clearly favors the formation of the cyclic monomers whereas that of a *trans*-double bond appears to promote the formation of the cyclic dimers. The combination of a triple bond with a *cis*-double bond always leads to a good yield of monomer.

At 2 x 10^{-3} M, formation of cyclic monomer is the dominant process and excellent yields are obtained in several cases. The presence of two unsaturations clearly help the formation of the C-11, C-12, C-13 and C-14 cyclic monomers by comparison with the mono unsaturated and saturated cases,[5-7] but this tendency is less important as the chain length increases to C-14. Further analysis of these results will require detailed molecular modeling studies.

This study shows the usefulness of unsaturations[8] in the synthesis of medium and large ring by direct cyclization under medium dilution conditions.

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3. The synthesis of these aliphatic chains will appear in a forthcoming detailed paper.
4. All spectra (250 MHz, ^{1}H and ^{13}C, 80 MHz ^{1}H nmr, ir and high resolution mass spectra) are in agreement with the assigned structures.
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