

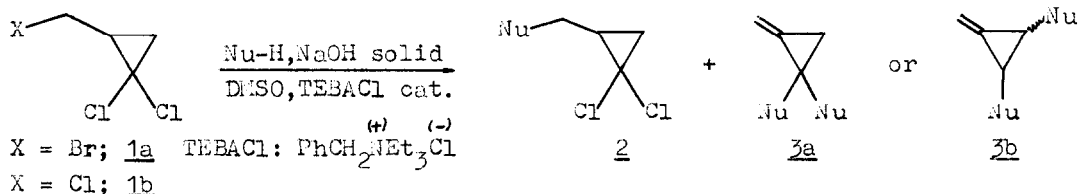
A NEW REACTION OF 1,1-DICHLORO-2-HALOMETHYLCYCLOPROPANES IN BASIC MEDIUM¹

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Summary: Utilization of the reaction of nucleophilic reagents with 1b allows for the simple preparation of methylenecyclopropane derivatives 3 via elimination-addition routes.

It has been reported² that 1a reacts with nucleophilic reagents (e.g. potassium phthalimide, sodium diethylmalonate) to give chain substituted products 2. We wish to report that the reactivity pattern of 1³ is strongly influenced by the nature of nucleophilic reagent and reaction conditions leading either to the formation of product 2, or a mixture of products 2 and 3.

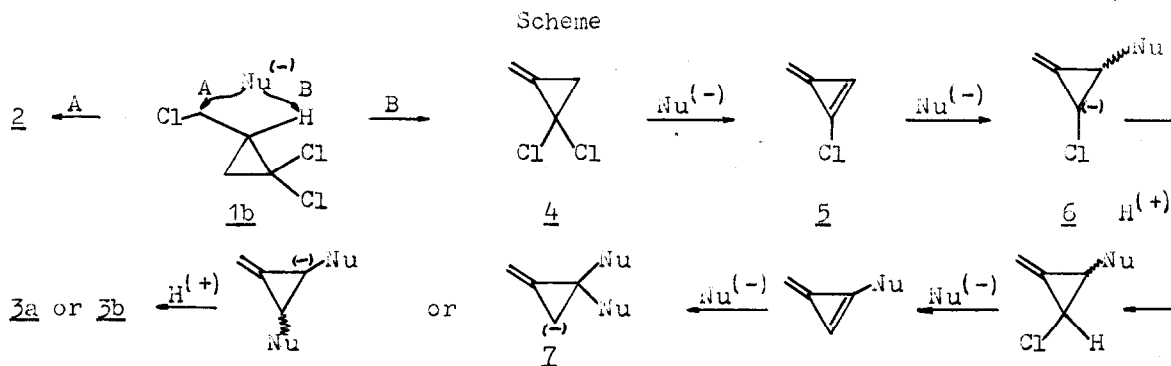


Nu-	Product(s) ^a		B.p. (°C/mmHg) m.p. (°C)	Nu-	Product(s) ^a		B.p. (°C/mmHg) m.p. (°C)
	No.	yield ^b (%)			No.	yield ^b (%)	
PhO-	<u>2a</u>	10	105-106/0.1		<u>2d</u>	9	107-110/0.05
	<u>3a</u>	73.5	94-96		<u>3b1</u>	88 ^c	163-170/0.05; 95-93
PhS-	<u>2b</u>	91	96-99/0.1		<u>2e</u>	34	150-152/0.01
PhCH ₂ O-	<u>2c</u>	74	135-133/0.01		<u>3b2</u>	46	145-143 (trans)

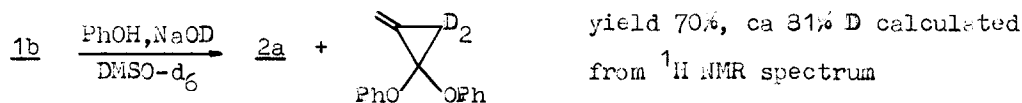
^a all compounds were fully characterized; ^b the yields were not optimized;

^c mixture of diastereoisomers, cis-trans stereochemistry not determined.

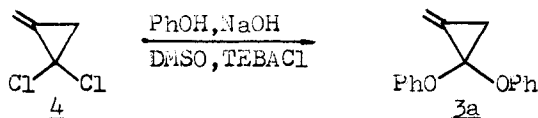
Clearly, the products 2 are formed via a S_N process (Scheme, path A). Analysis of the literature⁴ as well as the results of our experiments (see below) enable us to suggest that the formation of 3 proceeds via elimination-addition reactions (Scheme, path B).



The interaction of 1b which takes place with phenol in NaOD/DMSO- d_6 confirms that carbanions 6 and 7 are generated during the reaction course.



Methylenedichlorocyclopropane (4)⁵, a reactive intermediate reacts with phenolate to yield the anticipated product 3a⁶ according to Scheme, path B.



Our paper presents evidence for the intermediacy of substituted methylenecyclopropanes as reactive intermediates⁴. We have also described a new, simple procedure for the preparation of methylenecyclopropane derivatives.

REFERENCES AND NOTES

1. Reactions of Organic Anions, Part CIII: A. Jończyk, T. Pytlewski, J. Org. Chem., in press.
2. K. Steinbeck, Liebigs Ann. Chem., 920 (1979).
3. Qualitatively similar results were obtained both with 1a and 1b, only the results with 1b are described in this paper.
4. For recent examples see: W. E. Billups, A. J. Blakeney and W. T. Chamberlain, J. Org. Chem., 41, 3771 (1976), and literature cited therein.
5. T. Greibrokk, Acta Chem. Scand., 27, 3207 (1973).
6. 3a1: ^1H NMR (CDCl_3) δ : 1.59-1.76 (m, 2H, Δ), 5.14-5.61 (m, 2H, $\text{CH}_2=$), 6.55-7.11 (m, 10H, Ar-H); ^{13}C NMR (CDCl_3): 17.85 (t), 81.42 (s), 105.29 (s), 115.11 (d), 120.43 (d), 127.37 (d), 130.10 (s), 154.27 (s).

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