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A NEW REACTION OF 1,1-DICHLORO-2-HALOMETHYLCYCLOPROPANES IN BASIC MEDIUM[1]

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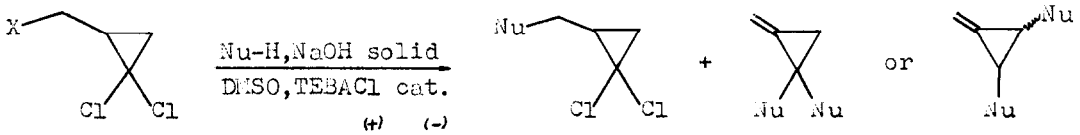
Summary: Utilization of the reaction of nucleophilic reagents with 1b allows for the simple preparation of methylenecyclopropane derivatives 3 via elimination-addition routes.

It has been reported[2] that 1a reacts with nucleophilic reagents (e.g.potassium phtalimide, sodium diethylmalonate) to give chain substituted products 2. We wish to report that the reactivity pattern of 1[3] 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.



X = Br; 1a TEBACl: $PhCH_2\overset{(+)}{N}Et_3\overset{(-)}{Cl}$ 2 3a 3b

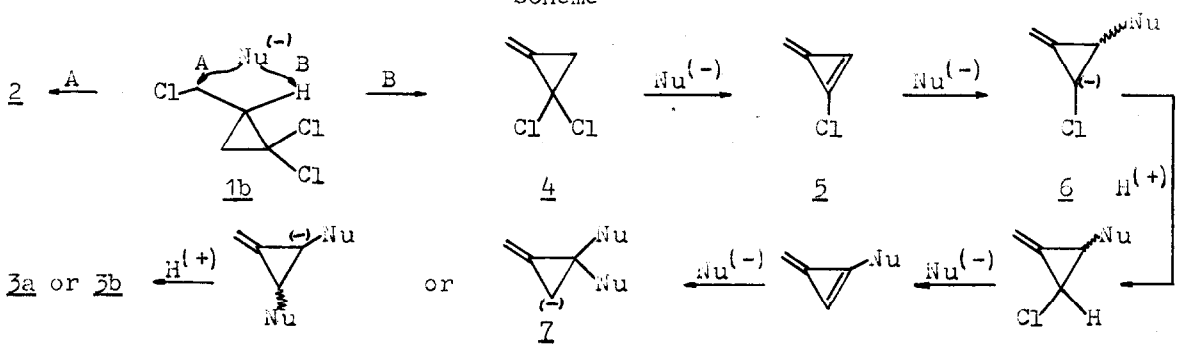
X = Cl; 1b

Nu-	Product(s)[a] No.	yield[b] (%)	B.p.(°C/mmHg) m.p. (°C)	Nu-	Product(s)[a] No.	yield[b] (%)	B.p.(°C/mmHg) m.p. (°C)
PhO-	2a	10	105-106/0.1	PhC(Me)(CN)-	2d	9	107-110/0.05
	3a	73.5	94-96		3b1	88[c]	168-170/0.05; 95-98
PhS-	2b	91	96-99/0.1	PhC(Ph)(CN)-	2e	34	150-152/0.01
$PhCH_2O$-	2c	74	136-138/0.01		3b2	46	146-148 (trans)

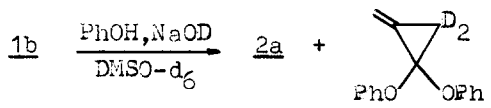
[a] all compounds were fully characterized; [b] the yields were not optimized; [c] mixture of diastereoizomers, cis-trans stereochemistry not determined.

Clearly, the products 2 are formed via a S_N process (Scheme, path A). Analysis of the literature[4] 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).

Scheme

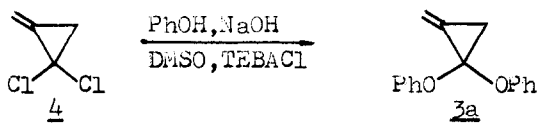


The interaction of 1b which takes place with phenol in NaOD/DMSO-d_6 confirms that carbanions 6 and 7 are generated during the reaction course.



yield 70%, ca 81% D calculated from ^{1}H NMR spectrum

Methylenedichlorocyclopropane (4)[5], a reactive intermediate reacts with phenolate to yield the anticipated product 3a[6] according to Scheme, path B.



Our paper presents evidence for the intermediacy of substituted methylenecyclopropanes as reactive intermediates[4]. 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: ^{1}H NMR ($CDCl_3$) δ: 1.59-1.76 (m, 2H, Δ), 5.14-5.61 (m, 2H, 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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